JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913+INCORPORATED 1914

Vol. 39 MAY 1953 No. 353

Contents

LIQUEFIED PETROLEUM GASES

Production. By E. S. Squire
Distribution. By S. Shaw
Utilization. By T. H. Taylor

The Structure of Lubricating Greases and its Control
By J. B. Matthews

Influence of Naphthalene on Octane Ratings
By G. E. Mapstone and J. S. Durham

The Metallic Elements in Residual Fuel Oils
By F. H. Garner, S. J. Green, F. D. Harper, and R. E. Pegg

Stability of Fuel Oil–Gas Oil Blends
By D. G. Butlin

Abstracts Book Reviews Additions to Library

Published by the Institute of Petroleum
26 Portland Place, London, W.1
Telephone No.: LANgham 2250
Telegraphic Address: Instpetech, Westdo, London
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk

Price 10s. 0d. Annual Subscription £4 14s. 6d. (Post Free)

COUNCIL, 1953–54

PRESIDENT

H. S. Gibson, C.B.E., M.A., M.I.Mech.E.

PAST-PRESIDENTS

Sir Andrew Agnew, C.B.E.
S. J. M. Auld, O.B.E., M.C., D.Sc.
T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
E. A. Evans, M.I.Mech.E., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
C. A. P. Southwell, C.B.E., M.C., B.Sc.

VICE-PRESIDENTS

E. B. Evans, M.Sc., Ph.D., F.R.I.C.
H. Hyams
J. A. Oriel, C.B.E., M.C., M.A., B.Sc., F.R.I.C.
H. E. F. Pracy, B.A., M.I.Chem.E.
R. B. Southall
G. H. Thornley, M.Sc.

MEMBERS OF COUNCIL

W. S. Ault, B.A.
V. Biske, B.Sc., LL.M., F.R.I.C.
C. D. Brewer, M.I.Mech.E.
E. J. Dunstan, M.Sc., M.I.Chem.E.
F. L. Garton, M.A., B.Sc.
A. J. Goodfellow, B.Sc., A.R.I.C.
A. C. Hartley, C.B.E., F.C.G.I., B.Sc. (Eng.), M.I.C.E., M.I.Mech.E.
E. LeQ. Herbert, B.Sc., F.R.I.C.
E. C. Masterson, B.Sc.
F. Morton, Ph.D., D.Sc., F.R.I.C.
J. S. Parker, M.A., B.Sc.
A. J. Ruthven-Murray, M.A., B.Sc.
D. L. Samuel, B.Sc., A.R.I.C.
G. H. Smith, Ph.D.
A. R. Stark, B.Sc., A.R.I.C.
E. J. Sturgess, B.Sc.
W. H. Thomas, A.R.S.M.
O. F. Thompson, O.B.E.
A. T. Wilford, B.Sc., F.R.I.C.
C. S. Windebank, B.Sc., M.S.

EX-OFFICIO

S. A. Berridge. Fawley Branch
A. W. Deller, D.F.C. London Branch
H. H. Ballard. Northern Branch
W. M. Stirling, A.H.-W.C., A.M.I.E.E. Scottish Branch
N. W. Grey. South-Eastern Branch
E. J. Horley. South Wales Branch

HONORARY SECRETARY: C. Chilvers, B.Sc., F.R.I.C.

HONORARY TREASURER: G. H. Coxon

GENERAL SECRETARY: D. A. Hough, A.I.A.C.

HONORARY EDITOR: F. H. Garner, O.B.E., Ph.D., F.R.I.C.

HONORARY ASSOCIATE EDITOR: E. B. Evans, M.Sc., Ph.D., F.R.I.C.

EDITOR: George Sell

HONORARY SECRETARIES OF BRANCHES

Fawley Branch: S. A. Berridge, c/o Esso Petroleum Co. Ltd., Fawley, Southampton.

London Branch: R. F. Leach, M.A., c/o Shell-Mex and B.P. Ltd., Shell-Mex House, Strand, London, W.C.2.

Northern Branch: G. M. Davies, c/o Esso Petroleum Co. Ltd., Mode Wheel Installation, Trafford Wharf Road, Manchester 17.

Persian Gulf Branch: G. A. Hogg, B.A., c/o Kuwait Oil Co. Ltd., Kuwait, Persian Gulf.

Scottish Branch: W. M. Stirling, A.H.-W.C., A.M.I.E.E., Scottish Oils Ltd., Middleton Hall, Uphall, Broxburn, W. Lothian.

South-Eastern Branch: F. A. Maliphant, c/o Anglo-Iranian Oil Co. Ltd., Kent Oil Refinery, Isle of Grain.

South Wales Branch: E. J. Horley, National Oil Refineries Ltd., Llandarcy, Glam.

Stanlow Branch: V. Biske, B.Sc., LL.M., F.R.I.C., Lobitos Oilfields Ltd., The Refinery, Ellesmere Port, Cheshire.

Trinidad Branch: H. C. Costelloe, c/o Apex (Trinidad) Oilfields Ltd., Siparia P.O., Trinidad, B.W.I.

THE INSTITUTE OF PETROLEUM

An Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 10 December 1952, the President, H. S. Gibson, C.B.E., in the Chair.

The President said: The symposium on liquefied petroleum gases being presented this evening consists of three papers by Mr E. Squire, assistant general manager (Technical) of National Oil Refineries Ltd., by Mr S. Shaw, who is distribution manager of the Calor Gas (Distributing) Co. Ltd., and by Mr T. H. Taylor, chief engineer of the same Company. All are members of the Liquid Fuel Gas Industry Committee, Mr Squire being the vice-chairman.

The following papers were then presented:

THE PRODUCTION OF LIQUEFIED FUEL GASES

By E. S. Squire * (Fellow)

Introduction

Liquefied petroleum gases are distributed in Britain for domestic and industrial uses.

For domestic purposes, the liquefied gas consists essentially of C_4 hydrocarbons, with small quantities of C_3 hydrocarbons, and with not more than about 1 per cent of the higher hydrocarbons.

For most industrial purposes, such as metal cutting, the liquefied gas consists essentially of the C_3 hydrocarbons.

The choice of hydrocarbons for the different duties depends mainly on the working pressure and the rate of offtake required from a given size of container.

For domestic purposes, the commercial butane has a vapour pressure of about 25 p.s.i.g. at average atmospheric temperatures, with a maximum vapour pressure of 85 lb at 45° C.

The commercial propane used for industrial purposes has a vapour pressure of approximately 100 p.s.i.g. at average atmospheric temperatures, with a maximum vapour pressure of 285 p.s.i.g. at 45° C.

Sources

The main sources of liquefied petroleum gases are natural gas, crude oil, gases from cracking and reforming processes, and the gases from hydrogenation processes.

In Britain liquefied gases are obtained from the last three sources.

In the case of crude oil, while the amount of butane or propane present might be small, the concentration in the gases or light distillates obtained from the distillation of the crude oil may be considerable.

* National Oil Refineries Ltd.

When conditions justify the procedure, and where butane is separated at the source of the crude oil production, as it frequently is, it has been possible to balance the market demand for butane in Britain by enriching the crude oil with butane up to approximately 6 per cent by weight without undue loss on transport. This has been found to be a convenient way of transporting butane from overseas.

Manufacturing Methods

The method employed for the recovery of liquefied gases will depend on its source, its composition, and the percentage recovery which is required or which is considered economically justified.

Considering what is probably the simplest manufacturing method, *i.e.*, recovery of butane from crude oil distillation, most modern distillation units are equipped with a primary flash column working at a pressure of up to 50 p.s.i. In this column up to 10 per cent of the crude oil is taken as distillate, and under the working conditions of the column all the lighter fractions, such as butane and propane, are condensed with this distillate, little or no gas being produced.

This distillate is passed to a stabilizing plant, from which stabilized gasoline with the required vapour pressure is produced, together with liquid propane and butane, and gas which is used as refinery fuel. The sequence of operations is determined by local conditions; in some cases the propane and butane are condensed together at the top of the stabilizing column and passed to another column in which the butane is taken as a residue and the propane either as a tray cut or, more frequently, as an overhead product.

Where the ratio of propane to butane in the crude oil is low and no propane production is required, it is sometimes possible to take specification butane as a liquid product overhead direct from the stabilization column, thus simplifying the operations and reducing the cost of production.

Where the propane and butane are obtained from gaseous sources such as natural gas or from most cracking operations, it is generally necessary to compress the gas to some pressure, depending on its composition. In the simplest processes the compressed gas is then cooled and a condensate is obtained containing liquid gasoline fractions, together with propane and butane, which are fractionated as previously described.

In some cases the gases at high pressure are passed through an absorption column, where the gasoline and lighter fractions are absorbed in a suitable absorption oil and recovered in a desorption column. The use of this absorption column usually results in higher yields or, alternatively, allows the process to be worked at lower pressures.

Where maximum yields of propane and butane are required, it is not unusual for the gasoline containing propane and butane to be passed to a de-ethanizing column where ethane is removed, to a depropanizing column for the recovery of propane, and then to a debutanizing column, in which butane is produced overhead and stabilized gasoline on the bottom of the column.

In recent years it has become fairly general practice to use refrigeration in the recovery of these gases in order to reduce the working pressures. Where the maximum propane recovery is required and a de-ethanizing step is included, the use of refrigeration makes it easier to separate methane

and ethane from the propane, due to a more favourable relationship between the vapour pressures of these hydrocarbons.

If very low temperatures are employed, it is essential that the feed materials should be thoroughly dried in order to avoid troubles arising from separation of hydrates.

Specifications and Test Methods

The salient points in the specifications for liquefied gases are intended to ensure that the whole of the contents of the container can be evaporated at the desired working pressure, under normal temperature conditions. This requires that there should be present not more than a small quantity of heavy ends, and that the pressure in the container should be adequate even at the lowest temperature likely to be experienced.

Difficulty arises here because, as the contents of the container evaporate, the liquid remaining contains progressively smaller proportions of the lighter hydrocarbons, as a result of differential evaporation. This is a particular difficulty in the case of liquefied butane for the domestic market in Britain, as the normal butanes boil at approximately 0° C and the *iso*-butanes at −10° C, temperatures which are very near the ambient temperatures that might be experienced in Britain. As the gas is used and the liquid becomes denuded of propanes, the pressure falls and may be too low to operate the pressure-controlling valve and the appliances. Where this becomes a serious problem, mixtures of propane and butane are marketed, and where very low temperatures are experienced, propane is used.

It will be appreciated that heat has to be supplied for the evaporation of the liquid. Part of this heat is initially supplied by the sensible heat of the liquid itself, but once equilibrium is attained, with continuous offtake of gas, this heat must be supplied from the atmosphere through the container walls. The rate at which gas can be taken from a cylinder is therefore largely determined by the area of the walls of the container and the difference in temperature between the container contents and the outside atmosphere.

Limits are also set to the proportion of the lighter hydrocarbons present, for example, ethane in commercial butane, as this can have a considerable influence on the burning characteristics of the gas.

The liquefied gas should be free from H_2S, and should not contain large enough quantities of mercaptans to produce a nauseating odour. On the other hand, it is essential that the liquefied gas should have a distinct and pronounced odour, so that if leaks occur they can be detected before the concentration in the atmosphere approaches the lower explosive limit. In some cases it is necessary to add an odorizer, and those commonly employed are alkyl sulphides and disulphides, mercaptans and certain concentrates from the re-running of turpentine. A limit is set to the total sulphur content to reduce the corrosive effect of the products of combustion.

Free water should be absent.

The analysis of liquefied gases is normally carried out in the Podbielniak or similar distillation apparatus. Approximate results, for control purposes, can be obtained by weathering tests carried out in a graduated glass cylinder, under roughly standardized conditions.

The Reid vapour pressure apparatus formerly employed for vapour pressure determinations was found to give low results, due to the solution, in the sample, of air from the air vessel and to the differential evaporation of the lighter hydrocarbons from the sample into the air vessel.

In the Reid apparatus the air vessel has a volume four times that of the liquid vessel, and in the case of liquefied gases having a high vapour pressure the amount of hydrocarbons evaporated into the air vessel became a large proportion of the sample.

Arising out of a request made by the Liquid Fuel Gas Industry Committee, the apparatus for vapour pressure determination is, therefore, being re-designed by the Institute of Petroleum. The modified apparatus is, in fact, an inverted Reid apparatus in which the larger vessel is filled with liquid and the smaller one is used as the air vessel, which, in the new method, will be purged with vapour from the sample before the determination of the vapour pressure.

It is also hoped that it will be possible to use the newly designed apparatus as a pyknometer for determining the density of liquid gases.

Storage

The design of storage vessels and containers is based on the pressure which will be reached at the highest temperature which is likely to be experienced in any given area. In Britain the temperature agreed upon is 45° C (113° F), so that butane containers are designed for a working pressure of 85 p.s.i.g. (100 lb abs) and propane containers for 285 p.s.i.g. (300 lb abs).

The bulk storage of butane may be in horizontal cylindrical tanks or, if large quantities are to be stored, in hortonspheres.

The maximum amount of liquefied gases which may be stored in a container is such that at a temperature of 45° C the volume of liquid must not be more than 95 per cent of the total volume of the container. This amount

Table I

Relation Between Filling Ratio and Density of Liquefied Gas at 15° C

Density at 15° C		Maximum Filling Ratio
Not Less than	Less than	
0·510	0·515	0·440
0·515	0·520	0·445
0·520	0·525	0·450
0·525	0·530	0·455
0·530	0·535	0·460
0·535	0·540	0·465
0·540	0·545	0·470
0·545	0·550	0·480
0·550	0·555	0·485
0·555	0·560	0·490
0·560	0·565	0·495
0·565	0·570	0·500
0·570	0·575	0·505
0·575	0·580	0·510
0·580	0·585	0·515
0·585	0·590	0·520

is defined by the filling ratio, which is the weight of liquefied gas it is permissible to store, divided by the weight of water which the container will hold at 150° C.

The filling ratio, therefore, is a figure which numerically is not greater than 0·95 times the density of the liquid at 45° C.

The density of these liquids is not easily determined by routine methods at 45° C, so that instead the filling ratio is related to the density of the liquefied gas at 15° C, as shown in Table I.

Filling of Containers for Liquefied Gases

Liquefied gases are distributed in Britain in a variety of containers of different capacities varying from a few pounds up to approximately 1 ton, and in rail cars with a capacity of 8 tons.

The containers are filled on a weighing machine, and great care is taken to avoid exceeding the filling ratio for which the container is designed.

In the case of commercial butane it is essential to remove air from the container as, if it is not removed, the initial offtake of gas containing large proportions of air will not burn in the burner. Air is usually removed by evacuating the container, then filling with butane gas to a pressure slightly above atmospheric to avoid leaks of air into the container while transporting from the evacuating point to the filling point.

In some cases the operation of evacuation and re-filling with butane gas is carried out twice, especially on containers which are known to contain large proportions of air, such as new containers being used for the first time, or those which are found to have been returned with the valve open or those from which the valve has had to be removed for some purpose or another.

After filling, the bottle and valve are tested for leaks by submerging under water, and the bottle is then sealed, and finally the weight of the bottle is checked before despatch.

DISTRIBUTION OF LIQUEFIED PETROLEUM GASES

By S. Shaw *

Although liquefied petroleum gases have been distributed in the U.S.A. for more than twenty-five years and in Europe for a period of upwards of twenty years, it was not until the completion of the hydrogenation plant built by I.C.I. Ltd. at Billingham that these gases became available in Britain for domestic purposes.

It is, therefore, safe to say that 1935 was the year which saw the birth of this now flourishing industry.

It was at first thought that the most natural medium for distribution would be the town gas industry, by its adding bottled or cylinder gas for use outside the sphere of gas mains. This method, however, did not prove to

* Distribution Manager Calor Gas (Distributing) Co. Ltd.

be successful, and other methods of making L.P. gas known in its rural market had to be adopted.

For a period of time direct canvassing of potential consumers was largely the practice of the industry, and it was not until 1937 that a more general system of enlisting the aid of local country businesses as dealers in L.P. gas was attempted. Even to-day, this procedure is not universal, as one distributor still employs the direct to consumer method.

The seventeen years during which the industry has been in operation can be divided up into three distinct periods; (1) pre-war; (2) war; and (3) post-war.

The pre-war period included an era of unemployment, trade depression, etc., with the result that the early pioneering days presented terrific problems in the promotion of what was then an unknown product. In spite of this, however, considerable success was attained. Sufficient at any rate to enable the industry to continue during the war period with gas distribution to its existing consumers.

Valuable assistance was also rendered to the war effort in many interesting spheres.

There was, however, no question of continuing any form of intensive sales campaign owing to the impossibility of securing supplies of steel for cylinder manufacture, or other raw materials required for the manufacture of butane gas appliances. Also the amount of L.P. gas available for distribution was limited—therefore little or no expansion was possible.

With the cessation of hostilities there was, however, a solid foundation on which has been built a very solid industry, playing a more than useful part in providing town amenities to people located outside the range of town gas —in many cases also outside the range of electricity, although in the latter case considerable progress has been made in meeting competition from the growth of the electric grid.

Such has been the growth, that to date it is estimated there are some 350,000 consumers in country homes, etc., in Britain dependent on L.P. gas supplies for cooking, heating, water heating, and lighting purposes.

From these figures it can be quickly estimated that, to date, upwards of 1,000,000 people, therefore, are in daily need of L.P. gas.

It has been mentioned that the initial source of supply was from I.C.I., Billingham, although supplies were shortly afterwards made available by National Oil Refineries Ltd. at Llandarcy. Supplies from Llandarcy, however, ceased on the outbreak of war, and were not resumed until 1945. During the war, therefore, supplies of L.P. gas for the whole of the United Kingdom were dependent on the one source at Billingham, and were distributed by rail transport, which was subject to the difficulties of wartime conditions.

Even during the war period, however, it was recognized by the various interested Government departments that the people dependent on L.P. gas for cooking, etc., formed a high essential need, and transport priorities were freely given, with L.P. gas enjoying the same priority rating as coal.

During the build-up for D-Day the industry was given very short notice, some fourteen days in all, in which to take away from rail transport all L.P. gas cylinders and to introduce road transport methods, as no rail transport would be available. A trunk road haula e system was introduced and

delivered cylinders of gas to selected depots for local road haulage redistribution. This distribution continued for the remainder of the war period.

Llandarcy came back into the picture soon after the end of the war, and L.P. gases became available for distribution, not only from Billingham and Llandarcy, but also from the " Shell " Refining and Marketing Co. Ltd. at Stanlow, the Esso Petroleum Co. Ltd. at Fawley, and Scottish Oils Ltd. at Grangemouth. These developments have been of the greatest possible assistance to all distributors in tending to simplify the resolution of transport problems.

Although there is a movement of L.P. gases by rail tank car, it can be said that for domestic purposes road transport is now universally adopted. This road transport movement might now be divided into two sections (*a*) where L.P. gas is collected from refineries in bulk road tank cars for delivery to a filling station for storage purposes and subsequent filling into suitably sized cylinders for domestic purposes, (*b*) where the greater part of filling into these smaller cylinders is carried out by filling stations inside the refineries and deliveries are in accordance with the requirements of the various distributors, either (i) direct to dealer; (ii) to depots for subsequent delivery to dealers; or (iii) to depots for subsequent direct delivery to consumers.

Mention has been made of suitably sized cylinders for domestic purposes, and the following is a brief description of the types more generally in use :—

1. *Locker cylinder*, having a 13-inch diameter base standing approx 12 inches high and containing 14 lb of L.P. gas.
2. *Normal domestic size cylinder*, also having a 13-inch diameter base with an overall height of approx 23 inches and containing 32 lb of L.P. gas.
3. *For large type installations*, cylinders containing 83 lb of L.P. gas have been introduced and those also have a 13-inch diameter base and stand approx 50 inches high.

With the increased growth of the industry, and including all types of distribution, there are at least 1500 points in Britain from which L.P. gas is available for local distribution to consumers.

For the most part, consumers' installations consist of two cylinders—one for use and one for reserve purposes—and under these conditions a continuity of gas supply can be guaranteed. The normal method to ensure a continuity of gas supply is for the consumer to advise the dealer or depot that the cylinder in use is exhausted and requires replacement.

Although complete statistics are not available, it is estimated that the average consumer use is about eight 32-lb fills per annum. Thus the dealer, or depot, has ample time in which to effect deliveries of gas in accordance with the consumers' requirements.

On the basis of there being approx 350,000 consumers and at an average use of eight 32-lb fills per annum, it will be seen that some 2,800,000 32-lb cylinders are distributed annually. As seventy of these cylinders make up 1 ton of gas, the industry is at present consuming in the region of 40,000 tons of L.P. gas each year.

With a view to improving conditions throughout the industry, and in order to ensure consumer safety and satisfaction, an Industry Committee

was formed in the year 1947 to include both producers and distributors and to provide liaison with cylinder manufacturers and appliance manufacturers.

On the distribution side, appliance manufacturers have improved the construction of L.P. gas appliances very materially, and with the introduction of codes of practice for fixing installations, the consumer interest has not been ignored and the general expansion of the industry has derived its best salesmen from existing satisfied consumers.

THE UTILIZATION OF LIQUEFIED PETROLEUM GASES

By T. H. TAYLOR *

GENERAL

Introduction

A DIVERSE and complicated machinery has been established for the purpose of ensuring the receipt by a customer of a fill of liquid gas. This paper attempts to describe without excessive detail the wide diversity of the applications of L.P. gas as a fuel; the attempts being made to raise the standard of utilization; the precautions taken by all concerned to ensure high efficiency and low risk to the customer. Finally, an attempt is made to look into the future and the conclusion drawn that, impressive as the growth of the L.P. gas business has been, it is merely the prelude to much wider application.

Historical Review and Official Bodies

The L.P. gas business has made enormous strides since first introduced into Britain in the middle nineteen thirties, and it is creditable that a technical body was formed nearly six years ago (*i.e.*, while the industry was still quite small) for the purpose of propagating the safe and efficient use of the fuel. This body, the Liquid Fuel Gas Industry Committee, will be well known to many, but the scope and importance of its work will not be so well known. Its membership includes all the major producing and distributing companies, and can rightly claim to be fully representative. Its programme of work covers the complete handling and utilization of L.P. gases, from the composition of the gas to the operation of the appliances; much useful work has been done.

To an extent probably not equalled by any other fuel industry the L.P. gas industry specifies and controls every item used, and as a result has a proud accident record.

Fortunately, or unfortunately, according to the point of view, no Government regulations exist which control the quality and performance of L.P. gases, and it is to provide such guidance as is necessary, and to anticipate

* Chief Engineer, Calor Gas (Distributing) Co. Ltd.

regulations, that the Committee exists. Specifications for all items of equipment are drawn up, either by the Committee or by the distributing companies, and the general standard improves steadily. As far as filling ratios and cylinder specifications are concerned, the Home Office, the National Physical Laboratory, and the Department of Scientific and Industrial Research have been instrumental in providing useful information and have treated the industry with fairness and sympathy.

The Ministry of Works has now started work on codes of practice for butane use, and work done by the LFGIC to date will be of special value to the committee being formed. Effective liaison with manufacturers' bodies, such as the Small Boat Builders' National Federation, the National Caravan Council, etc., has been maintained, and has culminated in the issue of documents covering codes of practice for butane installations in yachts and caravans. The BSI has a committee working on appliance performance; the initial documents for this committee were produced by one of the panels of the LFGIC. There is also close liaison between the LFGIC and the Institute of Petroleum for the purpose of producing standard test methods.

Applications

Domestic

Most people are familiar with such domestic equipment as cookers, fires, water heaters, lights, etc., and it is not proposed to examine them in great detail. The range of appliances available is rather smaller than that existing in the town gas industry, but it is true to say that practically every type of appliance in use in the domestic town gas industry has its counterpart in the L.P. gas business. It is a widely held, but erroneous belief, that most L.P. gas appliances are used in caravans and yachts. This is a very faulty assumption. Generally speaking, although the range of equipment available is as wide, the L.P. gas business is in an earlier stage of development than the town gas business, and a lower degree of saturation with appliances exists. Most installations started with lighting and/or a boiling ring, progressing through a hot-plate to a cooker. The water heater and refrigerator are recent entries to the market, and their full possibilities have not yet been exploited. The same applies to space heating. There are a wide variety of space heating appliances, ranging from the orthodox portable or fixed fire to the overhead radiant heater: the latter method has obvious advantages when using a high-priced fuel intermittently.

Caravans

Caravans present certain unique features. First, the question of vibration of pipes and joints in transit has to be considered; this also applies to lights, globes, mantles, etc. This means that special care must be taken in doing the job and designing the fittings. Certain physiological considerations arise from the low cubic capacities involved with these vehicles. Any fuel burned fluelessly in the presence of air vitiated with the products of combustion and respiration, will produce highly poisonous carbon monoxide. The remedy is to have adequate ventilation. Although this is primarily a question of caravan design, it has been tackled by the National Caravan Council only after full consultation with the LFGIC.

Agricultural

Broadly these installations are limited in application and are not widely used at present. Brooders and incubators represent a vast potential consumption of L.P. gases, on a variety of small applications. There are many thousands of small poultry breeders in Britain, and L.P. gas has many advantages over the fuel more commonly used at the moment. With the increased accent on hygiene in handling dairy products, sterilizing and pasteurizing equipment is more widely used, and by the very circumstances of its use presents a field for exploitation. Minor applications which have been successfully carried out include the heating of farrowing pens, pig food preparation, poultry house lighting for the stimulation of egg production, soil sterilizing, greenhouse heating, ovens for bacteriological research on soil, etc. Grain and crop drying on a small scale has not been attempted, and L.P. gas can only compete with fuel oil for this purpose under very special circumstances.

Commercial

It will be apparent that hotels, restaurants, country clubs, cafés, etc., are often situated far from public services, and it is under these circumstances that widespread use is made of L.P. gases. The convenience, cleanliness, and ease of control of the fuel lead to its adoption in place of solid fuels, and the remarks made regarding L.P. gas and town gas in the case of domestic equipment apply equally well here. Large scale cooking, water, and space heating represent a good load as yet little developed. Another field covered in this category is public lighting, and here L.P. gas is serving an ever-increasing number of traffic islands. The application to bollards, direction signs, etc., using fully automatic devices is rendering yet one more service in the cause of public safety.

Industrial

Oxy-flame cutting of metals, *e.g.*, at shipyards, represents a useful outlet for L.P. gases—primarily propane and propylene, and since the author's knowledge of this process is not obtained first hand, it will suffice just to mention this important use. Other industrial applications are, for use in heat treatment processes, paint drying, etc.

Semi-industrial

In this category come such uses as those employed in painting and decorating, small workshops, etc. An interesting application is in the use of a small steam unit, fired with L.P. gas for the stripping of paper from walls. Paint burning torches are widely used, and box and pig branding have also been accomplished. Steam raising and central heating have not been extensively applied, as the superior performance is of comparatively small importance against the much greater running costs involved. It is apparent that there is an optimum size for L.P. gas installation with prevailing prices, and this size is dependent upon the type of installation, the relative importance of fuel and labour costs, and the incidence of these costs in the cost of the final product.

Miscellaneous

Laboratory use is a good example of this type of application, and again the availability of a town gas supply is often the least important consideration in choosing a site for a laboratory. Building space in cities and urban areas is restricted, rates and the cost of amenities and labour are high, and the surroundings are not always conducive to research work. Under these circumstances there is a greatly increasing trend for large organizations to set up laboratories and research centres far from main gas supplies: here again L.P. gas comes into its own. The foregoing remarks apply specially to projects concerning the development of atomic energy, and L.P. gas is widely used in laboratories of this type. Wider small scale usage is found in workshops and garages for such jobs as brazing, soldering, lead burning, glass blowing, and in the dental and jewellery trades, for melting of precious metals, vulcanizing, etc.

Mobile

Mobile applications are specially suited to L.P. gases, and such vehicles as travelling dental and medical units, fish shops, laundries, etc., owe much to butane.

Equipment

Cylinders

The normal working pressure in the cylinder is of the order of 20 to 30 p.s.i., and the test pressure, depending upon type, 200 to 450 p.s.i. The bursting pressure is over 1000 p.s.i.g. The thickness of the shell is, in the case of butane cylinders, approximately $\frac{1}{10}$ inch, and for propane approximately $\frac{1}{8}$ inch. The cylinders are of two piece construction, consisting of two deep drawn pressings joined by a circumferential weld. The material is a mild steel of low carbon (0·2 per cent max), sulphur (0·05 per cent max), and phosphorus (0·05 per cent max), the ultimate tensile strength is up to 30 tons/sq. in., and the yield and elongation are closely specified. Part of the specified requirements concern the sampling of test cylinders and the tests to be carried out. These include a full metallurgical examination of one in every 200 cylinders, and a bursting test on a like number. The properties specified relate to both the raw material and the finished product, and the heat treatment is designed to achieve them.

Only qualified welders can be employed on the fabrication, and tests are laid down for the qualification of the welders. For protection of the cylinders, metal spraying and galvanizing are widely adopted; the cylinders are re-tested every three years, and regular inspection is carried out during their lifetime.

Ancilliary equipment (Valves, pigtails, wall blocks, regulators, etc.)

All the equipment coming in the high pressure category is rigidly examined by both manufacturers and distributors before despatch to the dealer and thence to the customer. There are three types of installation involved, the single, the twin, and the multiple cylinder. It is the normal practice to discourage the first, as the use of single cylinders reduces the time allowed

for replenishment, and leads to rather unsatisfactory operating conditions. The twin cylinder installation is normally employed on domestic work, and two methods are adopted for coupling these cylinders together, by use of a parallel connector or a wall block manifold. The parallel connector consists of a specially shaped ½-inch brass pipe fitted with a female inlet union at each end and a male left-hand threaded outlet at the centre. The wall block manifold consists of a wall block having ¼-inch B.S.P. inlet connexions and a male left-hand outlet thread, and two pigtail connexions with ¼-inch B.S.P. connexions at one end and a female union at the other. In all cases the cylinder valve to parallel connector or pigtail connexion is by means of a left-hand union nut threaded with a 14 T.P.I. metric thread. In the case of multiple cylinder installations the desired result is achieved in one of two ways, either by using multiples of the twin system or by making separate connexions from each cylinder and leading these into a combining manifold. The cylinder valve is subject to the same rigorous control in manufacture as every other piece of high pressure equipment, but in addition the valve is removed and completely reconditioned every time the cylinder is re-tested, or when damaged or failing to operate efficiently.

The regulators are of two types, first the low pressure which operates to reduce the inlet pressure from the average of 20 to 30 p.s.i. to, in the case of the Calor Gas Company, 11-inches w.g. The other is the high pressure regulator, which maintains outlet pressures from 0 to 15 p.s.i. as required. Both regulators are adjustable, and give acceptable performance over wide ranges of gas offtake and inlet pressure.

Installation

General

On the low pressure side the points to be considered are the piping, its sizing and method of installing, taps, fittings, etc. The most important aspect of this work arises from the necessity to use special L.P. gas-resistant lubricants and sealing compounds. It is, therefore, necessary that the work be executed by an operative informed about the properties of the gas, as well as skilled in the operations involved. Only approved materials should be used in the installation, and the distributing companies have in the course of years standardized on semi-annealed, solid drawn, virgin copper pipes and the special type of joint known as a compression joint. This does not preclude the use of steel or wrought iron threaded pipes, but when using these materials the jointing compound should satisfy, among others, the following requirements :—

(i) L.P. gas, water, and heat resisting;
(ii) non-corrosive;
(iii) uniform consistency and ease of application.

Lubricants should also be L.P. gas, water, and heat resisting, and be easy of application. In all cases it is the practice of the distributing companies to recommend suitable materials for lubricating and jointing.

Naturally, many problems are met in the utilization of the fuel, and none more pressing or important than that of training the installing engineer. Various methods have been used in the attempt to solve the

problem, all having their advantages and disadvantages. The Calor Gas Company instituted a training scheme at a company centre, but discarded this after two years in favour of the mobile training scheme which is now in force. Even supposing an operative is fully trained in the necessary fitting practices, it is still necessary for him to have some idea of the physics and chemistry involved in the use of the gas before he is fully capable of meeting eventualities on the spot. Problems blithely described as "short-life" gas, "excessive odorant," lack of vaporization, gas will not burn, etc., still remain to plague him; it becomes necessary for him to be able to talk intelligently about possible causes.

One of the problems encountered in utilization is that of maximum allowable offtake of gas. Since the vaporization of the gas depends upon heat transfer taking place between the ambient air and the liquid, and since this is dependent on many factors, it is not proposed to enlarge upon this, except to state that the consideration is complicated by the fact that the heat transfer is taking place through a continuously varying area (the area wetted by the liquid in the cylinder), and with a varying thermal capacity according to the intermittency of use.

It may be of interest to consider the manner in which an installation would be effected. First, the fitter would compute the load to the various appliances, and using established procedure, arrive at his pipe sizes and cylinder requirements. He would then decide upon the location of the cylinders, bearing in mind that it should conform to the following conditions:—

(i) be near to the point of greatest offtake;
(ii) be accessible for the changing of cylinders;
(iii) allow cylinders to be upright and give adequate clearance to operate the valves;
(iv) be shielded from extremes of temperature and from exposure to direct radiation from high temperature sources;
(v) be well ventilated and well away from sumps, drains, basements, etc.

The nature of the work undertaken is so important that the fitter spares no effort to ensure best possible results; among other things, great accent is placed on the necessity for courtesy in dealing with the customer. He must be fully conscious of the correct use and care of tools and observe the cardinal rules of craftsmanship. The installation completed, the fitter carries out a pressure test and instructs the customer in the operation of the appliances before regarding the job as completed. It is necessary also to instruct the customer on the method of operating the cylinder valve and of changing cylinders, although as the service provided becomes more universal each day, fewer customers need to perform this operation themselves.

Special

The special inquiry or installation is outside the scope of the normal dealer, and it is essential that his service be backed by a technical centre capable of advising on all his difficulties.

In addition to ensuring that the equipment provided is the best and cheapest the technical centre must continuously devote its energies to training by means of manuals, leaflets, etc.

Future Developments and Conclusions

Owing to the magnitude of the subject this review has necessarily had to be sketchy, but it would not be complete without some reference to possible future developments which are put forward on a purely speculative basis. It is apparent that improvement of equipment, extension of range of applications, and greater economy in distribution methods will lead to a greater use in the domestic field. The greater use of saturated and unsaturated hydrocarbons as starting points for an ever-increasing range of chemical products will lead to more absorption into daily life. The competitive position of L.P. gases as fuels *vis-à-vis* solid fuels and town gas and electricity is likely to improve as time goes on, and the outlook, therefore, is one of an expanding industry. As far as the future is concerned, the prospects are promising indeed.

Discussion

J. S. Wilding : The Liquid Fuel Gas Industry Committee was formed in 1947 as an association of the producers and distributors of liquid gases and has worked on a completely voluntary basis. The development of the liquid gas trade could have been very adversely affected by the random sale of a potentially dangerous product for use in unapproved installations, and it speaks highly for the good will and sound principles of the members of the industry that liquid gas holds the assured position it does to-day. The Committee is on the point of reorganizing itself to meet the growing demands on its services, under a new constitution which provides for a subscription from members and the installation of a permanent Secretary.

Coming to the papers themselves, I have little to say about Mr Squire's admirable précis of liquid gas production methods. Some remarks on the recovery of liquid gas from hydrogenation processes might have been interesting, but this is no doubt covered in the section on recovery from gaseous sources.

Incidentally, the hydrogenation process used by the ICI at Billingham, to which Mr Shaw refers, uses creosote as its raw material, the main product being gasoline, so that the liquid fuel gases from this source are from a non-petroleum, home-produced product. For this reason I would like to see the term " Liquefied Fuel Gases," as used by Mr Squire, or " Liquid Fuel Gas," as in the name of my Committee, appear in the title of this symposium and that of the other two papers. Similarly, " L.F." gases should replace " L.P." gases where the abbreviation is used.

One other point is the mention of lighter hydrocarbons, such as ethane, in commercial butane, by Mr Squire. I should have thought that an amount of ethane sufficient to give a noticeable effect on the burning characteristics of the gas would cause the product to be outside specification limits on vapour pressure. The point would, however, apply to commercial propane.

ANNUAL REVIEWS OF PETROLEUM TECHNOLOGY

VOL. 13 (covering 1951)

Published by the Institute of Petroleum
339 pp.

Price 50s. 0d. post free

TABLE OF CONTENTS

PETROLEUM GEOLOGY. By C. A. Fothergill. Origin of Petroleum—Migration and Accumulation—Sedimentation—Submarine Geology—Regional Tectonics—Search for Oil.

GEOPHYSICS. By D. T. Germain-Jones. Geophysical activity throughout the world—Seismic methods—Gravity methods—Magnetic methods—Other methods.

DRILLING. By E. E. de Bruyn. Rigs and rig equipment—Portable rigs—Marine drilling—Directional drilling—Drilling muds—Borehole operations—Well records.

PRODUCTION. By J. Birks and R. J. Davidson. Reservoir engineering—Reservoir control—Well engineering—Instruments.

TRANSPORT, STORAGE, AND DISTRIBUTION (1947-1951). By T. W. Mathias. Pattern of distribution—Transport—Storage—Pumps—Distribution—Prevention of Corrosion.

CHEMICAL AND PHYSICAL REFINING. By F. Morton. Sweetening and desulphurization—Acid treatment—Dehydration and desalting of crude oil — Absorption — Adsorption—Solvent extraction—Dewaxing and deasphaltizing—Refinery waste disposal.

CRACKING AND OTHER PROCESSES. By F. Morton. Cracking (New processes and experimental work — Description of plant—Location of Cracking units — Catalysts—Yields from cracking stocks)—Other processes (Alkylation—Isomerization—Thermal reforming, hydroforming and catalytic reforming—Polymerization).

DISTILLATION. By E. J. Charles. Equilibrium and other physical data—Distillation theory and calculations—Packed columns—Bubble-cap columns—Industrial units—Analytical and laboratory distillation—Vacuum and molecular distillation—Azeotropic and extractive distillations.

PLANT INSTRUMENTATION (1950-1951). By J. C. Farquhar. Graphic and Console Control Panels using Pneumatic control—Electro-pneumatic control systems—All-electric control systems—Monitoring systems and their control possibilities — Controllers, Control action, and interaction — Frequency response analysis — Flowmeters, flow controllers, and transmitters—Control valves—Analytical and quality control—Miscellaneous.

CHEMISTRY AND PHYSICS OF PETROLEUM. By J. N. Haresnape. Fundamental data (Composition of petroleum—Thermodynamics—Spectra and molecular structure—Vapour pressure and related properties—Distillation—Viscosity—Solubility—Other physical properties)—Physical Chemistry and Surface Phenomena—Synthesis—Reactions of Hydrocarbons (Alkylation and isomerization—Hydrogenation and dehydrogenation — Pyrolisis — Photolysis — Oxidation — Halegenation — Other reactions)—Combustion—Analysis—Sulphur compounds.

ANALYSIS AND TESTING. By J. Scott and A. G. Meredith. Crude oil—Gas—Gasoline and Kerosine—Gas, diesel and furnace fuels—Lubricating oils—Insulating oils—Asphaltic bitumen—Waxes and petrolatums.

NATURAL GAS, LIQUEFIED PETROLEUM GASES, NATURAL GASOLINE, AND HELIUM. By Thelma Hoffman. Natural gas—Liquefied petroleum gases—Natural gasoline—Cycling—Helium.

GASOLINE AND LIGHT DISTILLATES. By W. A. Partridge. Gasoline—Non-petroleum fuels and components—Kerosine, tractor oils and S.B.P.s—Gas-Turbine fuels.

LUBRICANTS. By D. L. Samuel. General review—Properties—Theories of lubrication—Engine lubricants—Bearing and gear oils—Metal-working oils—Refrigerator and compressor oils—Textile lubricants—Corrosion preventives—Greases—Non-petroleum lubricants—Additives.

INSULATING AND HYDRAULIC OILS (1950-1951). By C. N. Thompson. Insulating oils — Hydraulic oils — Patents.

PETROLEUM WAXES (1949-1951). By N. W. Gillam. Recovery and purification of waxes—Physical and chemical properties—Application tests of waxes—Commercial applications.

BITUMEN (1950-1951). By R. Hesketh. Composition and properties of bitumen—Bitumen emulsions—Problem of adhesion—Road applications—Industrial applications—Miscellaneous.

SPECIAL PRODUCTS. By P. Bailes, K. F. Coles and H. Kerner. Hydrocarbons—General chemicals—Polymeric products—Carbon black—Surface active agents—Petroleum coke and naphthenic acids.

OILS FROM COAL, SHALE, AND OTHER MATERIALS. PART I—HYDROGENATION AND SYNTHETIC PROCESSES. By P. G. Harvey and N. Levy. Hydrogenation—Fischer Tropsch Process.

OILS FROM COAL, SHALE, AND OTHER MATERIALS. PART II—DISTILLATION AND OTHER PROCESSES. By H. E. Newall. Low- and Medium-temperature carbonization processes—Oil shale—Bituminous tar sands.

OILS FROM COAL, SHALE, AND OTHER MATERIALS. PART III—HIGH TEMPERATURE CARBONIZATION. By K. H. V. French. Production at Coke-ovens and Gas-works — Gas purification — Benzole recovery — Refining — Other sources of aromatic hydrocarbons—Properties of constituents of Benzole—Storage and handling—Tests and Analysis.

PETROLEUM LITERATURE. By G. W. Dorrell. Exploration and exploitation — Transport and storage — Refinery operations and processes—Safety—Corrosion—Fuels—Lubricants and lubrication—Engines and engine performance of fuels and lubricants—Bitumen and road-making—Chemical Products—Waxes and fatty materials—Analysis and testing—Rheology—Petroleum (general)—Miscellaneous—Bibliography.

UNITED KINGDOM PETROLEUM LEGISLATION. By V. Biske. Taxation of petroleum—Conveyance of petroleum—Safety precautions—Customs regulations other than those arising from Finance Acts—Price and other controls—Trade disputes—Miscellaneous—Judicial decisions—References—Effects of 1951 petroleum legislation on earlier legislation.

PRODUCTION AND REFINING STATISTICS.

EXTRACTS FROM PRESS REVIEWS OF PREVIOUS VOLUMES

". . . of value to anyone desiring a ready means of tracing the progress of the industry."—*Petroleum Engineer.*

". . . an invaluable source of first reference to students, research workers and those many busy people in the industry who must keep abreast of the tide of events."—*Journal of the Institute of Fuel.*

"No laboratory or library dealing seriously with petroleum or any of its derivatives or products should be without this most valuable and condensed source of information and reference."—*Journal of the Institution of Engineers (Australia).*

". . . useful to every organization dealing with any of the phases of petroleum technology."—*Chemical and Engineering News.*

". . . contain much useful information and deserve a wide circulation."
—*Industrial Chemist.*

". . . a necessity to all who value their library on petroleum and its allied subjects."—*Scientific Lubrication.*

ORDER FORM

To **The Institute of Petroleum,**
26, Portland Place,
London, W.1, England.

Please send..... copy / copies of Vol. 13 of "Annual Reviews of Petroleum Technology" to

PLEASE ENCLOSE REMITTANCE WITH ORDER

(Signed)

In the paper on the distribution of L.P. gases, Mr Shaw gives a figure of 40,000 tons per annum for present consumption in the U.K., which, as he says, refers to commercial butane for domestic purposes. The total sales of liquid gases (butane and propane) are to-day about 48,000 tons per annum, the difference between this and Mr Shaw's figure being gas used for industrial purposes, to which Mr Taylor has made a passing reference.

A point on which I should like to enlarge a little is the difference in application of the two products. Propane has a considerably higher vapour pressure, and hence a greater output is obtainable from a container in a given time. The amount of propane available is much less than that of butane and is likely to be so in the future. It is, therefore, reserved mainly for industrial applications such as metal spraying and metal cutting with oxy-propane flames, which require sustained gas flows at a fairly high rate. Butane can deal with normal domestic requirements, and its lower vapour pressure allows larger quantities to be carried in thinner and lighter containers than propane, with appreciable advantages to the distributor and the domestic user.

These gases are sold by the different distributors under brand names—commercial propane as " Propagas " or " Pyrogas," commercial butane as " Butagas," " Calorgas," " Bottogas," and " Scottish Rural Gas."

During the last few years the gas boards in the U.K. have taken an interest in butane for use in small districts where coal gas supply is uneconomical. They have experimented with both a butane–air mixture and with butane-enriched water gas, and both have given very satisfactory results. A butane–air mixture having a calorific value of about 730 B.Th.U/cu. ft. has been distributed in the Whitland area of South Wales since January of this year, this system having the advantage that the plant is very simple and requires a minimum of maintenance. It was necessary, however, to modify existing appliances to use the gas, owing to its high specific gravity. At Spenborough, in Yorkshire, a small plant has been installed comprising a water gas generator and a butane mixer, the amount of added butane being automatically controlled to give a constant calorific value of about 450 B.Th.U/cu. ft. This plant has worked now for about eighteen months, giving a gas very similar in specific gravity to town's gas and capable of being burned in existing gas appliances. Butane for these appliances is drawn direct from the container in liquid form and converted to gas in a heated vaporizer, so that there is no dependence on container pressure for an adequate gas flow. These experiments are likely to lead to a considerable use of butane by the gas industry.

Dr E. Kroch : I understand that 40,000 tons of butane are being distributed each year in the U.K. for domestic use by about 350,000 consumers, an average of about 250 lb each. The amount distributed in Belgium is 48,000 tons per annum to about 600,000 customers, an average consumption of about 150 lb.

The proportion of the total population of Belgium living outside the gas mains is about 45 per cent, *i.e.*, some 3,750,000 people or 1,250,000 households as potential customers for butane. Of those, about one-fifth would be unable economically to purchase the gas, so that the number of potential

customers becomes about 1 million. I should be interested to know the proportion of potential customers in the U.K.

In the U.S.A. the domestic consumption is about 1500 lb per user per annum, supplied mainly in bulk.

I do not think that a name used worldwide for twenty-five years should be changed now.

MR SQUIRE : We prefer the term " liquid fuel gases " as " liquid petroleum gases " can be shortened to " L.P. gases," and in the minds of the public that is converted to " low pressure gases," which they are not. The LFGIC has thrashed this out many times.

A. L. WACHAL : When L.P. gases were first introduced in Poland, the problems were immense, and it is surprising that some of them have hardly received consideration by the authors.

In spite of the high propane content of marketed petroleum gases, the syphon-tube method for discharging containers was necessary in order to secure the gasification of these products under the severe conditions of East Continental winters. The latent heat had to be supplied at, or near, the pressure-reducing valve ; hence it was necessary to provide discharging equipment of special design, often embodying separate heat exchanging arrangements. From the last two papers it would appear that this problem is non-existent in the U.K., which is surprising because there are places here where the weather is not much better than that of mid-Europe.

So far as the design of L.P. gas burning appliances is concerned, I feel that Mr Taylor did not give full credit to gas engineers. In some applications it is not so easy to simulate the performance of town's gas by petroleum gases. The calorific value of these gases is up to seven times as high as that of town's gas, and the requirement of air may exceed even this proportion. Hence, there is need for very small and accurately calibrated gas jets and relatively high working pressures to facilitate the air induction at a sufficient rate. In comparison with coal gas, petroleum gases have a very low and highly temperature-dependent rate of flame propagation, and produce lower flame temperatures. I know of a case where a temperature of 1300° C for a heat treatment oven was very difficult to attain without resorting to preheating of the air.

Mr Taylor has told us about numerous very interesting applications of L.P. gases. There is, however, one important point missing, *i.e.*, how does the price of, say, 1000 B.Th.U. obtained from L.P. gases compare in the U.K. with the same amount of heat obtained from commercially available liquid fuels ? Also, I should be glad to know whether any attempt has been made in Great Britain to use L.P. gases as a motor fuel, at least in such a special application as on motor yachts, where a supply of gaseous fuel is required in any case.

MR TAYLOR : One of the subjects on which we have been intensely engaged has been the calibration of jets of from 5 litres per hour flow up to 100 litres per hour flow, which is the range normally used in the domestic side of the business. Jets can be, and are being, made with a flow tolerance of $\pm 2\frac{1}{2}$ per cent, which on a 5-litre jet is very close indeed. They

are being made by mass production methods, and there are producers in Britain who can make 10,000 jets a week to that accuracy.

I am not particularly well versed in the differences of flame temperature of the various gases. I was under the impression that the temperature attained with butane in a Bunsen burner was much the same as with town's gas, and I would put them both at about 1700° C. I am willing to accept what Mr Wachal has said about that, but my experience leads me to think that you will have considerable difficulty in getting a 1700° C working temperature without preheat. The only furnaces I know which are working at anything approaching these temperatures are such as the Davis reverberatory or crucible furnaces of very small capacity and very high heat release.

The normal prices for butane in Britain vary from something like 2*s* 6*d* to 3*s* 6*d* per therm. Kerosine, at 1·7 or 1·8 therms per gallon, costs the domestic consumer about 2*s* per gallon, or maybe more; so that the equivalent costs are 1*s* 1*d* per therm for paraffin and from 2*s* 6*d* to 3*s* 6*d* per therm for butane.

The only really statistical market survey of the substitution value of butane for kerosine in the U.K. was made in a rather limited area. It was established reasonably conclusively that the replacement value was 3 lb of butane (about 60,000 to 63,000 B.Th.U.) to a gallon of kerosine (175,000 B.Th.U.). So that it would appear that the utilization efficiency, for domestic purposes anyhow, is of the order of three times as much when using liquefied gas, as with kerosine.

As to the use of L.P. gases as a motor fuel, our Company is one of the largest distributors, and until quite recently we have been living hand-to-mouth in respect of both gas cylinders and equipment. One motor car can consume in a year as much gas as twenty or thirty or even a hundred domestic customers, and we would much rather keep our domestic customers. There is no real problem involved. No doubt all who are here know of the work done in the U.S. on the subject and of the vast amount of usage on traction there.

MR SHAW: In reply to Dr Kroch, so far as the potential market in Britain is concerned, it is similar to that in Belguim. When we started we estimated that there were about a million potential consumers.

As to the utilization of butane for traction, or at any rate for motor car propulsion, I would only comment that there are far too many gentlemen here who are anxious to sell petrol rather than butane.

A. W. RICHARDSON: It is quite wrong to assume that you can burn butane with so much higher efficiency than kerosine as has been stated.

MR TAYLOR: I was quoting figures given by a rather large distributor of kerosine. I was claiming that the appliances were something approaching three times as efficient when burning butane as when burning kerosine, and I was suggesting that people who use kerosine appear to be wasting a lot of it.

N. G. MACGREGOR: I should like to ask one or two questions about the use of propane and to have an analysis of it, with particular reference to the proplyene content.

In view of the statement that approximately 40,000 tons of butane are sold in Britain per annum, and bearing in mind atmospheric temperatures we experience, particularly in the north, where there may be many degrees of frost, I should be glad to know the percentage of residual liquid returned in the bottles, as it is appreciated that in cold weather conditions complete removal of butane is difficult. Could the authors tell me the incidences of fire or explosion as the result of burning propane, butane, or propane–butane mixtures, and also the incidence of personal injury or death?

MR TAYLOR : With regard to accidents, the industry has an extremely proud record. In the LFGIC meetings we have considered the hazards to a very considerable extent. We were under the impression, for example, that to put butane or propane into yachts was rather hazardous. However, in the course of our deliberations we called in an underwriter, representatives of yachting bodies, and interested Government Departments, and we asked what they thought about it. The underwriter was very worried, but about petrol, not gas ! The Government bodies, as is so often their wont, said that when we had produced something concrete they would look at it and say whether or not they liked it. The yachting fraternity were very unwilling to design a ship around a cylinder. So that we did not get very far.

However, we have obtained figures which prove quite conclusively that the number of accidents is infinitesimal. I think that in 1951 there were five accidents, and there were 2,800,000 cylinders sold in that year.

The only thing I can say about the amount of liquid returned is that it is returned to the filling station.

K. R. GARRETT : Commercial butane may be any mixture of C_4 hydrocarbons, including butadiene, which poses some combustion problems. It is hoped that in the next two years, when certain firms put in more plant, that constituent will be eliminated. In one part of the country the gas will be 90 per cent unsaturated C_4 hydrocarbons with possibly 10 per cent of butanes. In another part, the gas may consist entirely of saturated hydrocarbons. These mixtures may contain anything up to 20 per cent of propane, depending on the limiting vapour pressure, which, for small cylinders 2·5 mm thick, is 100 p.s.i.a. at 45° C.

For special purposes, *e.g.*, where there are extremely cold conditions, the proportion of propane can be increased to 50 per cent. For specific purposes, 100 per cent commercial propane can be used. The heavier types of cylinders will carry anything up to 100 per cent of propane.

The unsaturated hydrocarbon content depends on refining processes. Straight distillation of crude oil produces wholly saturated hydrocarbons. The C_3 hydrocarbon stream from such a process can contain as much as 97 per cent of propane, the remainder being ethane and butane.

On the other hand, cracking processes produce varying mixtures of unsaturated and saturated hydrocarbons. Regarding propylene, the Wilton plant is so designed that it will produce the max amount of ethylene and propylene. One can obtain a mixture containing up to 70 per cent of propylene, which is far better for cutting than is propane.

As to other ingredients in the gases, the total sulphur in commercial butane is limited to 0·02 per cent by weight, which is equivalent to 23 grains

of sulphur per 100 cu. ft. of gas at S.T.P. In general, the actual amount is less than half this figure, and it is very much lower than the average sulphur content of town's gas. The C_5 hydrocarbons, which tend to be left behind in the bottles in cold weather, are limited to 2 mol per cent. The caustic soda, which is used in washing the gas, is reduced to a very small amount, and hydrogen sulphide, which causes corrosion of steel, a crystallization effect, is reduced to nil.

E. E. Blandon : I was hoping to hear something about the work which I know is being done in the laboratories of Mr Taylor's Company on methods of measuring the combustion quality of the gas.

It was suggested by Mr Wilding that there are faint hopes of getting more propane, or of having a greater proportion of propane to butane in mixtures, and I wondered why there seemed to be much more propane in France, even to the extent of using propane–air for distribution in town gas mains.

In reference to the advantages of butane–water gas as against butane–air, the lower specific gravity has, of course, an advantage in itself, purely as a physical factor, but it is the effect of the hydrogen chemically, on the flame speed, which is the principal factor in making butane–water gas a much easier fuel to burn.

R. L. Messent : Mr Squire mentioned that supplies of butane from refineries and stabilizing units abroad were now being transported to the U.K. by injection in stabilized crudes. How much butane can be transported in this manner and approximately what losses are involved during transit ?

Could Mr Squire give his views on the future supplies of butane and propane available in the U.K. for liquid gas usage, as it now appears that surplus H_4 and H_5 hydrocarbons, which provide one of the main sources of supply for the liquid gas industry, are being utilized at refineries as feed stocks for processes such as isomerization with alkylation, and polymerization with hydrogenation, for conversion into high octane spirits for motor fuels.

The isomers of these H_4 and H_5 hydrocarbons are also finding an important outlet as raw materials for the manufacture of solvents, dyes, synthetic resins, plastics, synthetic rubber, detergents, etc., in the petrochemical industry.

Mr Squire : It has been possible to transport crude oil containing 6 per cent by weight of butane. This is possible by stabilization and removal of practically all the propane and the lighter constants, so that the enriched crude oil still has a vapour pressure of 10 lb Reid or less. Roughly, for every part of propane removed, six parts of butane can be introduced. The loss in transit is not higher than with normal crude oil.

With the commissioning of new cracking plants in the U.K., I think that the proportion of C_3 to C_4 hydrocarbons which will become available to the market will be increased. It is true that a large proportion of these unsaturated hydrocarbons may be used in a polymerization process for the production of high octane motor spirit. On the other hand, I think I am right in saying that, in the U.K., oil is specially cracked to produce the unsaturated hydrocarbons required for chemical manufacture.

DR KROCH : Nobody seems to have answered the question concerning supplies of propane being larger in France than in the U.K. The simple reason is that there is considerably more butane available in France than in the U.K. France now produces about 180,000 tons of butane, and has a potential production of some 120,000 tons of propane per annum.

The question of combustion characteristics and interchangeability of various fuel gases has been discussed very thoroughly in a paper which has been presented by Association Technique de l'Industrie du Gaz en France, and presented at the 5th International Gas Conference held in Brussels.

A. D. MAKOWER : In setting up a laboratory in a place a long way from a town's gas supply, liquefied petroleum gases can be used for bench burners. For most work this causes little inconvenience, but there are certain tests, specified by the BSI, etc., where specially regulated flames are required. The sort of tests I have in mind are the crucible swelling number for coal and inflammability tests for fabric and non-inflammable substitutes for rubber. In these instances closely standardized flames are essential, and I should like to ask whether in trying to use these gases for these specialized purposes one is aiming for the impossible or whether it is possibly, by use of suitable burners, to match performance with tests carried out with ordinary town's gas.

I should like to know also if ordinary pipelines with normal gas fittings are suitable for laboratory use and, in particular, if one reducing valve is considered sufficient for the large pressure reduction.

MR TAYLOR : Specialized tests can be done with butane. I am sure we have devised a piece of equipment for the coal swelling test. The determination of the inflammability of rubber is done by what I think is an Air Ministry test, using a high pressure blow-torch of a certain shape and size to heat the rubber to a specified temperature. I think there are very few standard tests which cannot be so modified as to cope with the normal variations of propane–air or butane–air flames, and if Mr Makower is in any difficulty in this matter I suggest that he consults one of the distributing companies.

For pipelines, any material normally used in town's gas practice can be used, with adequate safeguards. The town's gas industry does not use compo pipe ; so that you would not use compo pipe for butane–air. Ordinary wrought iron, galvanized iron, copper, and composite tubing can be used with the right fittings. Moreover, threaded joints can be adopted, provided the right jointing material is used. Indeed, there is very little limitation on the types of materials employed.

About reducing valves : we call them " regulators," and the gas industry calls them " governors." The extent of their use will depend on the lay-out of the laboratory, on whether it is more suitable or economic to run a high line around the laboratory and reduce the pressure at the benches, or to have a regulator at the cylinder bank and distribute at low pressure from that.

The pressure that can be obtained is many times greater than with normal town's gas practice. You can have almost any combination of pressures and any lay-out for pipelines and, except in unsatisfactory installation

conditions, you can be sure that you will get the pressure you require at each piece of equipment.

DR G. E. WILSON : I believe that the Calor Gas Company were working on the design of a gauge suitable for recording the volume of liquid in a cylinder. I would be glad to know what progress has been made in this attempt to devise a method of ascertaining the contents of a cylinder other than by difference weighing.

MR TAYLOR : We tackled this problem from all points of view—mechanically, by direct weighing, magnetically, electrically, and hydraulically—and applied all the principles we could think of. There are three sound methods : (1) a direct weighing machine; (2) an internal float; and (3) by pressure. You can obtain an indication of the contents by means of pressure, provided the pressure gauge has an adjustment on it so that it can be adjusted to the ambient temperature. There are quite a lot of these types of instruments in being. It is not so much a question of design as of economics, of the cost involved, because in a twin-cylinder installation you are not very interested in the contents; you simply replace a cylinder. The cost of a weighing machine is up to £6, and nobody wants to buy it. Particularly, the use of a float gauge is hopelessly bound up with the fact that there are in existence in the U.K. something over a million cylinders, which we cannot withdraw in order to cut holes in them and put in gauges.

Vapour pressure is about the only basis which really has promise, involving an ordinary dial pressure gauge which can be calibrated with a movable dial, which is set to the ambient temperature at the time of operation. The work is still proceeding.

DR KROCH : I am extremely interested and, shall I say, intrigued by the statement made by Mr Taylor that the actual contents of a domestic L.P. gas cylinder can be ascertained by measuring the vapour pressure. Obviously, there is some relation between the corrected vapour pressure and the quantity of L.P. gas remaining in the cylinder, and, quite logically, that vapour tension will decrease with the remaining liquid becoming richer in C_4 hydrocarbons, and poorer in C_3 hydrocarbons. However, so many factors are involved that it appears extremely difficult, not to say impossible, to establish a direct relation permitting even a rough estimation of the liquid remaining in a cylinder. The original composition of the L.P. gas and the rate of withdrawal would have to be identical at all times, in order to arrive at a definite correlation between the vapour pressure, and the quantity of L.P. gas remaining in the cylinder.

MR TAYLOR : I did not make myself quite clear. I was speaking of what is essentially a butane–propane mixture within specified limits of offtake. We have heard from Mr Squire how the percentage of propane gradually disappears as the content of the cylinder is reduced. It is quite possible, and has been demonstrated, that as the amount of gas in the cylinder is reduced the amount of propane present is reduced, and the pressure at any fixed temperature falls according to the content.

DR KROCH : I do not see how this can be done without taking into account the rate of withdrawal.

MR TAYLOR : The speed of withdrawal is obviously a point to be borne in mind. But 10,000 tons are supplied for industrial use and 40,000 tons for domestic use, *i.e.*, 80 per cent for domestic use, where the rates of withdrawal are the same, within extremely narrow limits. There may be a cooker only. It will not work where there are three or four fires and a cooker. But we are dealing essentially with simple installations, and I think that, even if you could not guarantee the operation of a particular pressure gauge over a wide variety of rates of offtake, it would be sufficient to give the customer adequate indication of the approximate quantity of gas left.

J. G. HANCOCK : I have not experience of liquid petroleum gases, but I have been told that it is quite easy to tell when a cylinder is becoming empty, because the smell increases.

MR TAYLOR : That is quite true. It is due primarily to the slight increase in concentration of the stenching agent towards the end of the cylinder.

MR RICHARDSON : If we are fair, I think we should say that this is a problem in the industry.

MR TAYLOR : Replying further on the subject of indication of contents by pressure : the application can be demonstrated. It will operate over a range from 10 to about 40 cu. ft/hour, which is equivalent to 30,000–100,000 B.Th.U/hour, and will give adequate indication. One does not expect to see recorded on the dial that there is 2 lb left. All that one wants to know is that the cylinder is a quarter full or a quarter empty. The customer merely wants adequate time in which to order a new cylinder.

MR V. BISKE : The level of the frost mark on the cylinder is surely at just about the level of the contents, and a reasonably accurate indication of the amount of liquid remaining.

THE PRESIDENT : I am sure you will all wish to join with me in thanking Messrs Squire, Shaw, and Taylor for having given us a most interesting symposium on liquid fuel gases. There is no doubt that the availability of these gases is a great blessing indeed to those who live in isolated dwellings, and in remote villages, and one can only hope that the industry can expand so that it can soon fulfil all needs. It may be necessary, as one speaker has mentioned, that in order that more people may use this fuel the price should be reasonable, possibly lower, than it is at present. But the greater consumption may introduce a problem in regard to supply, as the carrying capacity of imported crude oil for these gases is fairly limited. The expansion of refining in the U.K. will be of great assistance, of course.

One can appreciate, however, that the liquefied fuel gas industry undoubtedly has a very important future before it. I invite you all to join with me in thanking the three gentlemen who have given us this most interesting symposium.

(The vote of thanks was warmly accorded.)

THE STRUCTURE OF LUBRICATING GREASES AND ITS CONTROL*

By J. B. Matthews †

Summary

Recent work concerning the structure of conventional lubricating greases, made from soaps and hydrocarbon oils, is discussed, and it is concluded that greases consist of two phase systems, in which the soap and oil form two distinct phases. The soap exists in greases in the form of fibres, which interact together to form aggregates. The properties of the grease are dependent on the state of aggregation of the fibres, but with given components the properties of the grease are dependent on the length : diameter ratios of the fibres.

By controlling the phase structure of the oil–soap system during the period of fibre growth in the manufacture of lithium greases, it is possible to control the length : diameter ratio of the fibres, and hence to control the properties of the grease.

Introduction

Discussions on grease usually include remarks about the " art " of grease-making and the desirability of making a close scientific study of the subject, in order that the manufacture of greases can be put on a sound basis. Such remarks are rapidly becoming out-of-date, as a result of the considerable amount of scientific activity concerning the structure of lubricating greases, which has occurred during the past fifteen years. The results of this activity have led, not only to a better insight into the structure of lubricating greases, but also to a more scientific control of their manufacture.

The knowledge we now possess in this field has been accumulated during the last fifteen years by numerous independent workers, and the purpose of this paper is to attempt a co-ordination of their various results, and to present these in a way which reveals the modern views concerning the structure of lubricating greases made from soap. In addition, the paper also describes how this new knowledge has been applied to improvements in the manufacture of lithium greases.

Pioneering Work of A. S. C. Lawrence

Lawrence [1, 2] made an extensive study of the gels formed by many metal soaps in hydrocarbon oils, and recorded the changes in phase structure which occurred in these systems as the temperature was varied. In general, he found that, as the isotropic solution of soap in oil was cooled, gelation occurred at a temperature which he designated T_1; and at a lower temperature, which he designated T_2, a transition occurred from a clear gel to an opaque system. According to Lawrence, the clear gels are basically similar in structure to true solutions, since the two components, soap and oil, together form a single phase, and if the concentration of soap is too low,

* A paper based on a lecture delivered to the Northern Branch of the Institute of Petroleum on 19 February 1952.

† The Shell Petroleum Co. Ltd., Thornton Research Centre.

a solution with anomalous viscosity is formed instead of a gel. At the same time, however, he describes gelation as being a " crystallization," and states that " The soap separates suddenly and in a peculiar crystal habit, so that a meshwork is formed holding the oil like a sponge." The explanation offered by Lawrence for this paradox is that the crystallization of soap in the gel is inhibited at a very early stage, because the hydrocarbon chains of the soap molecules in the very small crystals are in the liquid state, the soap itself being in the swollen plastic phase stable between T_1 and T_2. Crystal growth, therefore, can only take place unidirectionally, in the plane of the carboxylate groups. However, if there is absence of cohesion between the hydrocarbon chains, it is difficult to understand how the long macromolecular threads can interact to form the meshwork necessary for the formation of a gel. On the other hand, it is easy to visualize Lawrence's thread-like soap micelles mixing with hydrocarbon oils to form liquid systems with high, anomalous viscosities, possessing no yield values.

The phase transition occurring at T_2 is, according to Lawrence, from the gel to a " pseudo-gel," or paste of fully crystalline soap suspended in oil. The crystals in this paste are very small to begin with, but grow larger on ageing. With a sufficiently high concentration of soap, the system is plastic, behaving as a Bingham body ; at low soap concentrations, however, the soap segregates.

Lawrence finally concludes that some greases are gels (according to his own definition of a gel) and that others are microcrystalline pastes. Furthermore, he adds that it is not really possible to state which sort of structure is desirable, the answer to this question being probably dependent on the applications to which the grease is to be put.

Further Developments in Phase Structure Work

Following these exploratory investigations made by Lawrence, the phase structures of oil–soap systems have been systematically studied by several people, notably by Vold and his collaborators. Whereas Lawrence's approach to the subject was largely qualitative in character, and most of his observations were visual observations of structural behaviour as the temperature was varied, the subsequent work has been largely quantitative, and specialized experimental techniques have been devised with which to make the observations.

Vold's work in this field has been mainly an extension to non-aqueous systems of the classical work carried out principally by McBain on the structure of solid soaps and their aqueous solutions. McBain and others had already shown that soaps can exist in different crystalline states, transitions from one phase to another occurring as the temperature is raised, until finally the soaps completely melt into the true liquid state. In addition, when water is added to soap to form a two-component system, McBain found that the phase behaviour was markedly affected, according to the relative proportions of the two phases. In the extension of this work to non-aqueous systems, various experimental techniques have been used for observing the transformation temperatures, and a few words about these experimental techniques would perhaps be appropriate at this stage.

Lawrence used the cooling curve technique to some extent, in order to

measure his phase transformation temperatures. This technique is the well-known method for determining melting points by plotting the temperature as a function of time as the system freely cools under constant external conditions. The rate of cooling is then proportional to the difference in temperature between the cooling system and its surroundings, and a smooth logarithmic curve is obtained when the temperature is plotted against time, so long as no phase transformation involving latent heat occurs during cooling. If such a phase transformation does occur, then, of course, a break is found in the cooling curve, and the corresponding temperature is the phase transformation temperature. The cooling curve method is not very sensitive, and can only be used satisfactorily to detect phase transformations which are associated with fairly large latent heats. For many of the transformations which occur in soaps and oil–soap systems, the latent heats are too small for the cooling curve method to be applicable, but in these cases a much more sensitive technique, known as differential thermal analysis, can be successfully applied.

Differential thermal analysis is a technique first applied by Le Chatelier [3] in 1887 to the study of phase changes in clays. Since then, the technique has been developed and used extensively in the study of clays and other minerals, and more recently in the study of catalysts used in the cracking of petroleum. Its application to soaps and greases belongs to the last decade.

The principle of the method is fairly simple and straightforward. Essentially, the apparatus [4] consists of two identical cells, each containing one junction of a thermocouple, the e.m.f. from which can be measured by a simple electrical circuit. One cell contains the soap or grease, or oil–soap system, and the other cell contains a comparison material, such as the lubricating oil component of the grease, which undergoes no phase transformations in the temperature range to be investigated. If both cells are immersed in an oil bath, the temperature of which is slowly raised at a uniform rate, the temperatures of the two cells rise equally, until a phase transformation occurs in the soap or grease. Then, owing to the latent heat of the phase transformation, a temperature difference between the cells is produced, which is recorded by the e.m.f. produced in the thermocouple. By plotting the e.m.f., or temperature difference, against time a thermogram is obtained, showing a peak whenever a phase transformation occurs (see Fig 1, which shows the results obtained with naphthalene in one cell and a lubricating oil in the other). If at the same time the actual temperature of the soap or grease is recorded, then it is possible to read off directly the temperature at which the transformation occurs. It can also be shown that the area enclosed by the peak, under standardized conditions, is proportional to the latent heat of the transformation,[4] and this information can be very useful for obtaining a more detailed understanding of the phase transformations which occur.

As already stated, the principle of this technique was first employed by Le Chatelier for measuring the temperatures of phase transformations in clays, but the apparatus and experimental conditions which are suitable for clays are very different from those which are suitable for soaps and greases. The main difference is that for minerals it is desirable to use fairly rapid rates of temperature rise and fall, whereas much slower rates are necessary in the case of soaps and greases.

The differential calorimetric method of thermal analysis just described can only detect thermal transitions which involve a latent heat. It is known, however, that phase transformations can occur, which do not involve latent heat. These phase changes, known as transformations of the second or higher orders, can be detected by making use of other properties, *e.g.*, viscosity, dielectric constant, infra-red absorption, and X-ray diffraction. In each case, the phase transformations are marked by sudden changes in the physical property concerned, and therefore, by measuring the

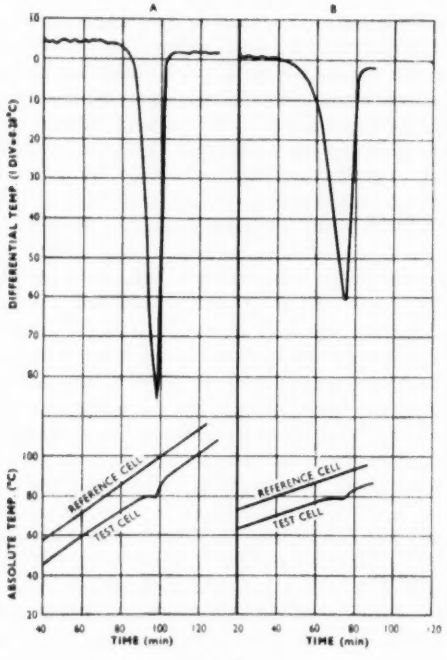


FIG 1

THERMOGRAMS FOR NAPHTHALENE, WITH RATE OF HEATING : A, 0·67°/MIN; B, 0·34°/MIN

property as the temperature is varied, the temperatures at which the phase transformations occur can be readily observed. Changes which can be visually observed, such as changes in texture, or changes in opacity, can also be used to determine transformation temperatures. Generally speaking, however, the majority of the phase transformations which occur are of the first order, *i.e.*, they involve a latent heat, and hence the differential calorimetric method is usually applicable.

By measuring the transformation temperatures for systems of varying compositions, phase diagrams can be constructed. Thus, Doscher and Vold,[5] and Smith and McBain [6] have published phase diagrams of mixtures of sodium stearate with various hydrocarbons, from which it appears that the phase behaviour of these relatively simple systems is quite complex.

It may be comforting to the grease manufacturer, however, to note that, in the soap concentration region in which he is mainly interested, *i.e.*, from zero to 25 per cent wt, the phase diagram is fairly simple, and the number of phase transitions which occur when the temperature is raised is relatively small.

In contradiction to the above results, Stross and Abrams [7] claim that if extreme care is taken to exclude moisture, the phase diagram for sodium stearate in cetane is much simpler than that given by Doscher and Vold. On the other hand, in the low soap concentration region, a greater number of transformation were observed by Stross and Abrams than by Doscher and Vold. The reason for these reported differences probably lies in the different experimental techniques used, since Doscher and Vold based their conclusions on visual observations of phase changes, whereas Stross and Abrams used the differential calorimeter technique.

The information which has been obtained concerning the different phases which can exist in any given oil–soap system is interesting for its own sake, and also because it strongly suggests that many of the phenomena which are familiar to the grease manufacturer, such as the differences in the final properties of the grease produced by differences in rate of cooling or rate of stirring, are probably explicable in terms of the phase transformations which occur during the temperature cycles followed in the manufacturing process. Thermal analysis techniques, obviously, can provide useful information concerning the crystalline structures which the soaps can assume in greases under different conditions of temperature and concentration, but, apart from throwing light on the soap phase structure, they do not carry us much further forward in forming a true picture of the structure of greases.

Micrographical Studies on Greases

The microscope in its various modifications is probably the most powerful tool which has been used in elucidating the structure of greases. Some of the earliest recorded photomicrographs of greases are those published by Farrington and Davis.[8] Using a dark-field, light microscope, and magnifications up to about 1000 ×, they examined a number of greases and found that the soap existed in these greases in the form of matted fibres of varying lengths. They claimed that a definite relationship existed between the length of the fibres and the texture of the grease, and proposed that all greases should be classified into four groups, designated as long fibre, medium fibre, short fibre, and microfibre, the corresponding grease textures and fibre lengths being :—

100 μ	fibrous, ropy texture;
10 to 100 μ . . .	clinging, slightly rough texture;
1 to 10 μ . . .	slightly rough, short texture;
1 μ	smooth, unctuous texture.

This classification has not been generally adopted, and very little notice appears to have been taken of Farrington and Davis's observations. The advent of the electron microscope a decade later, however, renewed the interest in the fibre structure of greases, and one of the pioneers in the application of the electron microscope to greases was the same Farrington who had made the earlier observations with the light microscope.

Several electronmicrographs of the soap fibres in greases have been published within the last ten years,[9–12] and these provide detailed pictures of the various structures which the individual soap fibres in greases can assume. It is almost inevitable, after looking at a sufficient number of such electronmicrographs, to imagine that a grease consists simply of a random dispersion of these extremely small, individual, soap fibres throughout the oil phase. It is important, however, to realize the limitations of the electron microscope before interpretating the data which it provides. First, in most cases the fibres have been separated from the grease before they are examined. Secondly, it is very difficult to obtain good pictures of the fibres *in situ* in the grease, because there is not a big difference in the stopping powers of hydrocarbon oil molecules and the long hydrocarbon chain soap molecules. Thirdly, when the soap fibres are separated from the greases, or when the hydrocarbon oil is replaced by some other liquid, it is probable that changes occur in the way in which the fibres are arranged with respect to each other. Finally, the field of view in the electron microscope is very limited, and therefore it is difficult to obtain with it a reliable picture of the macroscopic structure of the grease. In other words, the electron microscope, whilst undoubtedly providing us with valuable information concerning the structure of the individual fibres, cannot tell us much about the way in which the fibres are arranged in the grease to build up the macroscopic structure. In order to learn something on this subject, it is necessary to turn to the light microscope.

As in the case of the electron microscope, it is not easy to see the soap structure in greases directly with transmitted light, because of the similarity in the refractive indices of the soaps and hydrocarbon oils. With dark-field illumination, or preferably with polarized light, however, it is possible to obtain a fairly good idea of the manner in which the soap is dispersed throughout the oil phase, although it is not possible, of course, to see the individual fibres as one does with the electron microscope, since these are too small to be resolved. Thus, the fibres observed by Farrington and Davis in the dark-field microscope are almost certainly not individual soap fibres, but are probably aggregates of fibres.

The manner in which the aggregation of the soap fibres may occur in an oil–soap system is illustrated in Fig 2, which shows the changes which occur when a lithium stearate hydrocarbon oil system gelates. It will be noted that the gel structure, as distinct from the grease structure, appears to be associated with a secondary aggregation of the primary aggregates to form what may be described as giant fibres. Thus, different regimes of structure can apparently occur in oil–soap systems, and it appears that it is the manner in which the primary soap fibres are built up into superstructures which largely determines the bulk properties of greases.

Further Experimental Data Concerning the Structure of Greases

From the micrographical evidence, it is apparent that the soap present in greases exists in the form of discrete fibres, forming a separate phase from the oil, and that the properties of the greases depend to some extent on the manner in which these fibres interact. Confirmation of this two-phase

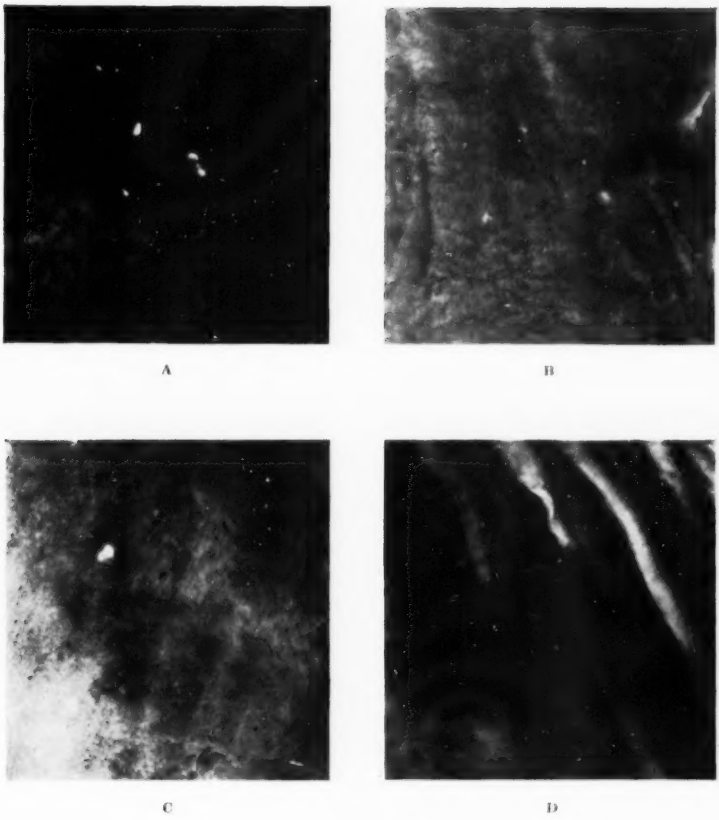


FIG. 2

CRYSTAL GROWTH DURING EQUILIBRIUM OF LITHIUM STEARATE GEL AT 110° C: A, 0 HR; B, 1·25 HR; C, 4 HR; D, 6 HR

Original magnification, 350 ×, crossed nicols

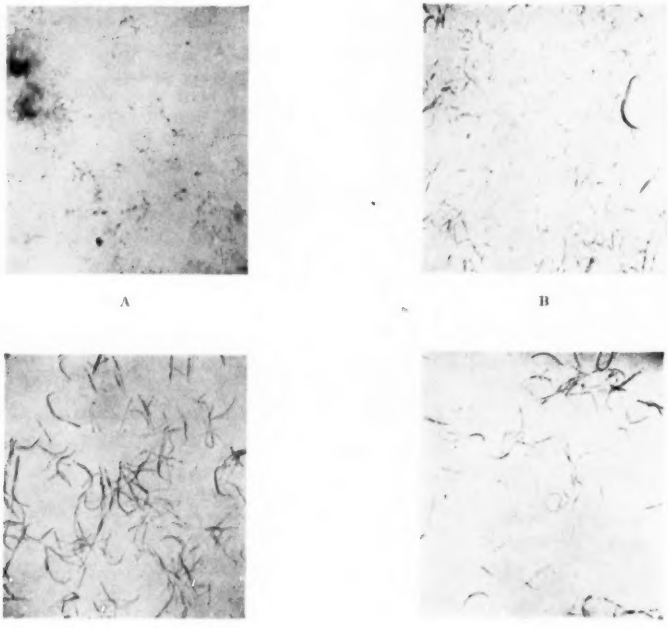
[*To face p.* 270.

A B C

FIG 6

FIBRE GROWTH DURING EQUILIBRIUM OF LITHIUM STEARATE GREASES AT 100° C: A, 0·5 HR; B, 1·5 HR; C, 2·0 HR

Original magnification, 5600 ×



A B C D

FIG 7

INFLUENCE OF EQUILIBRIUM TEMPERATURE ON GROWTH OF FIBRES IN LITHIUM STEARATE GREASES DURING EQUILIBRIUM FOR 2 HR AT: A, 210° C; B, 150° C; C, 100° C; D, 90° C

Original magnification, 5600 ×

structure of greases is provided by the experimental data published by Browning.[13]

Browning found that the oil phase in a grease could be replaced by a different oil by a simple process of washing the first oil away by the second. When this was done, the consistency of the grease was practically unchanged, even when the second oil was completely different in chemical structure and properties from the original oil. The inference to be drawn from this is that the arrangement of the soap fibres had not been disturbed by replacing one oil phase by the other. On the other hand, the softening caused by pushing the grease repeatedly through a 250-mesh screen was found to be dependent on the nature of the oil phase present. This may be interpreted as meaning that the equilibrium arrangement of the soap fibres is determined to some extent by the nature of the oil phase. Thus, although it is possible to replace gently the original oil phase by a different one without disturbing the original arrangement of the fibres, the forces of interaction between these fibres have presumably been altered by changing their environment. Hence, after being shaken up by the screen treatment, the fibres settle down again in a different arrangement, corresponding to a different degree of hardness of the grease.

Bondi, Cravath, Moore, and Peterson [12] found that, if a grease was subjected to prolonged shearing, mechanical degradation of the soap fibres could occur. This usually took the form of breakage along the short axis, to give shorter fibres of unchanged diameter, *i.e.*, a reduction in the length : diameter ratio. When the length : diameter ratio had been reduced to a low value, however, breakage then sometimes occurred along the long axis, to give an increase in this ratio. For a given grease, they found a relationship between the consistency (or hardness) and the length : diameter ratio, a decrease in the latter causing a softening of the grease. Indirect confirmation of this observation was obtained by mixing nylon filaments, cut to different length : diameter ratios, with lubricating oil, and measuring the consistencies of the suspensions. For a given concentration of nylon the consistency was found to decrease with decreasing length : diameter ratio.

Controlling the Structure of a Grease in Manufacture

The position at this stage may be summarized by the following statements on the structure of lubricating greases made from soaps :—

(1) Greases are essentially two-phase systems, consisting of dispersions of soap in oil.

(2) The soap generally exists in greases in the form of very small fibres, usually possessing a fairly large length : diameter ratio.

(3) The properties of the grease are largely determined by the manner in which the fibres interact with each other, but for a given grease composition the length : diameter ratio of the fibres plays an important part.

(4) All soaps, which are of interest from a grease manufacturing point of view, undergo phase transformations in the solid state, when the temperature is raised from room temperature to the final melting point.

This knowledge alone does not enable one to control the manufacture of a grease, but it has been possible to apply it, as the following example shows, to discover how effective control can be achieved. The example chosen is that of the manufacture of lithium greases.[4]

From the thermal analysis results for various suspensions of lithium stearate, lithium hydroxystearate, and their mixtures in lubricating oil, the phase diagrams given in Figs 3 and 4 were obtained. The shaded areas are those in which the tie-lines can be drawn.[4] It will be noticed that the values obtained for the transformation temperatures during cooling are in some cases quite different from those obtained during heating. For example, one lithium stearate transformation occurs at 180° C on heating and at 120° C on cooling. This supercooling effect can be repro-

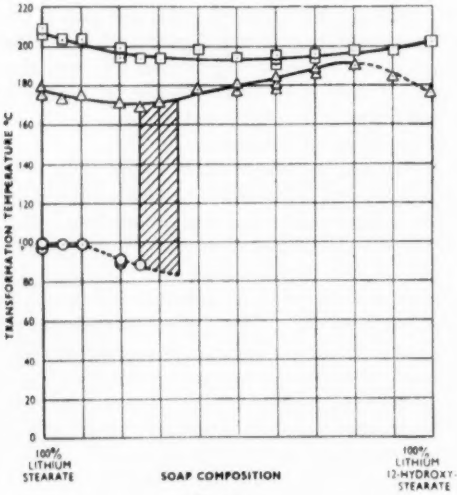


FIG 3

PHASE DIAGRAM FOR LITHIUM STEARATE–LITHIUM 12-HYDROXYSTEARATE GREASES —HEATING TRANSFORMATION

duced, but the reason for it is not known. In addition, four phase transformations are observed for lithium stearate systems on cooling between the final melting point and room temperature, but only three during heating. The explanation for this, deduced from latent heat data,[4] is that the highest heating transformation really consists of two phase transformations, which become resolved on cooling, owing to a difference in supercooling effects. In the case of the lithium hydroxystearate system there are only two phase transformations during heating or cooling. From the results obtained with mixed soaps, shown in Figs 3 and 4, it is obvious that the two upper transformations of the four observed for the stearate correspond to the single upper hydroxystearate transformation, and similarly, the two lower transformations of the stearate correspond to the single lower hydroxystearate transformation.

The next step was to investigate how the properties of a grease could be

modified by bringing the oil–soap system into its equilibrium state in each of its phases, and then rapidly cooling the system to room temperature. Greases made in this way from a given oil and a given concentration of soap were found to vary considerably in their properties, according to the phase state in which they were equilibrated, as illustrated in Fig 5. In those systems showing the four stearate-type transformations, the maximum hardness, as measured by ASTM penetration value, and stability, as measured by oil separation, are obtained when the system has been equilibrated in the phase which is stable between the two lower transformation temperatures. On the other hand, in the case of the systems showing only the two hydroxystearate-type transformations, the maximum hardness and stability appear to be

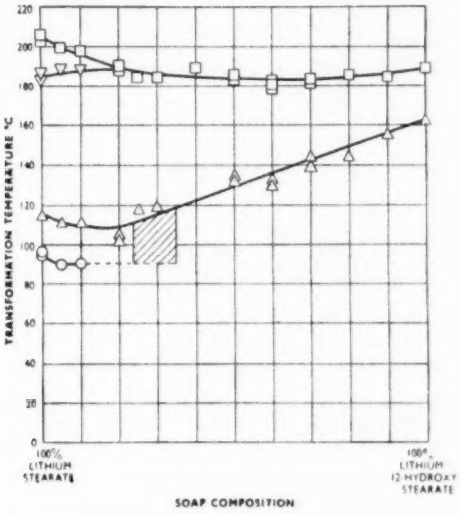


FIG 4

PHASE DIAGRAM FOR LITHIUM STEARATE–LITHIUM 12-HYDROXYSTEARATE GREASES —COOLING TRANSFORMATIONS

obtained when the equilibration temperature coincides with the lower transformation temperature. The latter result is not unexpected if considered together with the observation that the lower hydroxystearate-type transformation apparently consists of the two lowest stearate-type transformations merged together.

It might be inferred that the results shown in Fig 5, *i.e.*, the variations of the hardness and stability with equilibration temperature, are due to "freezing into" the final grease the different soap phase structures in which equilibration occurred. This conclusion, however, would not be true, for the rates at which these particular phase transformations occur are rapid, whereas the process of reaching equilibrium in the chosen phase is lengthy.[4] Furthermore, when the final grease is thermally analysed, the lower transformations are observed during the initial heating, whereas they would be

expected to be absent, if the grease consisted of a "frozen" high temperature phase.

The actual process going on during the equilibration stage is fibre growth, as shown by Fig 6; and the extent to which the fibres can grow, depending on the phase which exists during the growth period, is shown in Fig 7.

The true explanation of the results shown in Fig 5, as revealed by the fibre geometry given in Figs 6 and 7, would, therefore, seem to be that the properties of the grease, other things being equal, depend on the length : diameter ratio of the fibres. This length : diameter ratio, moreover, can apparently be controlled by growing the soap fibres while the oil–soap system is in a predetermined phase. It is well known that crystalline

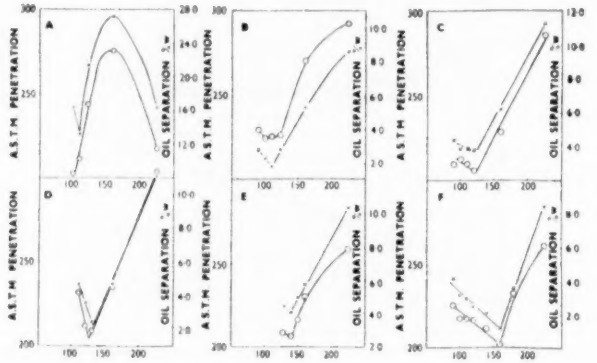


FIG 5

VARIATION WITH EQUILIBRIUM TEMPERATURE OF ASTM PENETRATION AND OIL SEPARATION FOR LITHIUM GREASES. RATIO OF LITHIUM STEARATE TO LITHIUM 12-HYDROXYSTEARATE BEING A, 100 : 0; B, 75 : 25; C, 60 : 40; D, 50 : 50; E, 80 : 20; F, 0 : 100.

X = ASTM penetration
O = oil separation

growth is dependent on the crystalline structure present, and therefore the result that different soap phases can lead to differently shaped fibres is not unexpected. Controlling the soap phase structure during fibre growth, of course, is but one way of controlling the fibre growth, and similar results should be obtainable by the introduction of additional substances into the system, as crystal growth modifiers. Similarly, the use of different oils may affect the fibre growth in different ways, as the result, perhaps, of the different surface-active impurities contained in them. For a given system, however, the results given in this paper indicate that the optimum grease properties and structure can be suitably controlled by paying due attention to the soap phase structure during the period of fibre growth.

ACKNOWLEDGMENT

The author wishes to thank The Shell Petroleum Co. Ltd. for permission to publish this paper.

References

1 Lawrence, A. S. C. *J. Instn Petrol. Tech.*, 1938, **24**, 207.
2 Lawrence, A. S. C. *Trans. Faraday Soc.*, 1938, **34**, 660.
3 Le Chatelier, H. *Z. phys. Chem.*, 1887, **1**, 396.
4 Evans, D., Hutton, J. F., and Matthews, J. B. *J. appl. Chem.*, 1952, **2**, 252.
5 Doscher, T. M., and Vold, R. D. *J. Colloid Sci.*, 1946, **1**, 299.
6 Smith, G. H., and McBain, J. W. *J. phys. Chem.*, 1947, **51**, 1189.
7 Stross, F. H., and Abrams, S. T. *J. Amer. chem. Soc.*, 1951, **73**, 2825.
8 Farrington, B. B., and Davis, W. N. *Industr. Engng Chem.* (*Industr.*), 1936, **28**, 414.
9 Birdsall, D. H., and Farrington, B. B. *J. phys. Chem.*, 1948, **52**, 1415.
10 Sproule, L. W., and Pattenden, W. C. *Canad. J. Res.*, 1948, **26F**, 465.
11 Bondi, A., Caruso, J. P., Fraser, H. M., Smith, J. D., Abrams, S. T., Cravath, A. M., Moore, R. J., Peterson, W. H., Smith, A. E., Stross, F. H., White, E. R., and Wilson, J. N. "Developments in the field of soda base greases." *Proc. Third World Petrol. Congr.*, 1951 Section VII, 373.
12 Bondi, A., Cravath, A. M., Moore, R. J., and Peterson, W. H. *Inst. Spokesm. nat. Lubric. Gr. Inst.*, 1950, **13** (12), 12.
13 Browning, G. V. *Inst. Spokesm. nat. Lubric. Gr. Inst.*, 1950, **14** (1), 10.

NOTE ON THE INFLUENCE OF NAPHTHALENE ON OCTANE RATINGS

By G. E. Mapstone * (Fellow) and J. S. Durham † (Member)

Naphthalene preparations have appeared on the market regularly as "mileage improvers," etc., and they are a possible, though minor, constituent of some gasolines. One of these "improvers" was tried at the recommended concentration of one teaspoon per 2 gal of gasoline in a 1950 model Morris six-cylinder car, and was found to give no detectable improvement in mileage or performance on runs of 300 miles, involving both city and country driving and all types of terrain. In his extensive review of the knock characteristics of hydrocarbons, Lovell [1] does not list naphthalene, and no information on its octane rating could be gleaned from the available literature. The work reported here was therefore undertaken in an attempt to supply the deficiency.

Naphthalene, in various concentrations by weight, was dissolved in two different fuels, one a 60 O.N. reference fuel and the other a xylene–*n*-heptane mixture. The octane numbers for these mixtures, clear and leaded, were determined by the Motor and Research methods. These are presented in Table I.

Table I

Octane Ratings of Naphthalene Blends

Sample	Motor method				Research method			
	Clear	1·0 cc	2·0 cc	3·0 cc	Clear	1·0 cc	2·0 cc	3·0 cc
60 O.N. ref. fuel . .	59·9	73·8	80·6	82·8	59·9	73·8	80·6	82·8
1% naphthalene in 60 O.N. ref. fuel . .	61·6	65·2	68·8	77·0	61·7	69·5	75	80
3% naphthalene in 60 O.N. ref. fuel (approx O.N.) . . .	64	69	76	80	63	70	77	82
Xylene–*n*-heptane mixture	53·2	59·4	66·2	71·5	—	—	—	—
1% naphthalene in xylene–*n*-heptane .	54·7	60·2	66·6	71·5	—	—	—	—
2% naphthalene in xylene–*n*-heptane .	54·6	62·3	69·6	72·0	—	—	—	—
4% naphthalene in xylene–*n*-heptane .	53·7	62·8	69·2	72·6	—	—	—	—

With the 60 O.N. reference fuel, naphthalene was deposited on the venturi tube of the air-intake manifold and the fuel line from the carburettor. The octane numbers obtained would not, therefore, correspond to the original concentration of naphthalene. Efforts to eliminate the deposit in the manifold by raising the temperature of the air intake to 200° F were

* C.S.I.R.O. Coal Research Station. † National Oil Pty. Ltd.

unsuccessful. A notable feature was the decided loss of rating with the leaded samples.

No deposit occurred in the intake manifold with the xylene–*n*-heptane mixture and naphthalene, though some deposition was observed in the fuel line, that with the 4 per cent naphthalene mixture being fairly heavy. This may explain the drop in rating of the clear sample. In most other instances a small increase in octane rating was experienced in both clear and leaded samples.

Because of the limited solubility of naphthalene in the blends examined and consequent small differences in the octane ratings of the blends, accurate blending octanes cannot be obtained. However, the blending octane number of naphthalene is high, and appears to be of the order of 200 for the clear mixtures examined. The T.E.L. susceptibility of the naphthalene in the blend appears to be poor, in agreement with the generalizations drawn by Lovell for the lead susceptibility of aromatic hydrocarbons.

The results obtained showed that, if sufficient naphthalene was added to the gasoline to produce a noticeable effect on the performance, fuel line and carburettor blockages would almost certainly be experienced. In this respect, a highly aromatic gasoline would give less trouble than a paraffinic gasoline. The best that can be said for the naphthalene "mileage improvers," therefore, is that they would be equivalent to adding an equal amount of a high octane gasoline.

ACKNOWLEDGMENT

The authors wish to acknowledge with thanks the permission granted by the management of National Oil Proprietary Ltd. for the publication of this paper.

Reference

[1] Lovell, W. G. *Industr. Engng Chem.* (*Industr.*), 1948, **40**, 2388–438.

THE METALLIC ELEMENTS IN RESIDUAL FUEL OILS

By F. H. Garner,* O.B.E. (Fellow), S. J. Green,* F. D. Harper,* and R. E. Pegg *

Summary

Deposition of ash and corrosion, both major difficulties in the use of residual fuels in gas turbines, are due mainly to vanadium and sodium in the oil. Iron, sodium, vanadium, and nickel are the chief metals present in an Iraq residue examined, and methods have been developed for the determination of these elements in oils. Iron and sodium compounds can be removed by filtration and water-washing respectively, but vanadium and nickel compounds cannot be removed by simple means, and are present as organic compounds dispersed in the oil. Adsorbent and solvent extraction have been found to concentrate the vanadium compounds, but by both methods the maximum for an Iraq oil was only fourteen times that of the original fuel oil, viz., 0·07 per cent vanadium. Both vanadium and nickel compounds could be concentrated in a fraction representing about 5 per cent of the Iraq crude used and in about 20 per cent of a Venezuelan crude, and they are combined with a significant part of the asphaltenes. Previous work suggesting that all the vanadium is present as porphyrins is criticized. No method was found of preparing fuel oils free from vanadium which would be cheaper than distillation.

Introduction

Gas turbines for ship propulsion, for land transport, and for power generation must be able to burn relatively low-cost residual fuel oils rather than the higher cost middle distillates which are the preferred fuel for air transport. The fuel oils should preferably be of high viscosity from which the middle distillates have been partially or wholly removed. Handling and combustion of such fuels are much more difficult than for middle distillate fuel oils, but nevertheless even highly viscous fuel oils can now be burnt efficiently. The major difficulty is not in the combustion process, but in the deposition of ash and the corrosive attack on the surfaces of the combustion chamber and turbine blades. The refining processes to which crude oil is subjected produce distillates free from ash but concentrate the ash-forming constituents in the residues. The constituents responsible for ash formation are inorganic, and are present in comparatively low concentration, normally less than 0·1 per cent. It has been shown that deposits in the gas turbines are similar in composition to the ash of the original fuel oil and that the two elements, vanadium and sodium, play a particularly important part in the deposition and corrosion.[1] Since both these elements are present in almost all crude petroleums, the problem appears to be of widespread importance.

As far as deposition is concerned, sodium appears to be more important than vanadium, and Lloyd and Probert [2] suggest that sodium pyrosulphate, vanadium pentoxide, and sodium vanadates act as bonding agents. Deposition is, however, usually accompanied by corrosion, which is particularly serious at high temperatures. This was shown, for example, by Schlapfer,

* Department of Chemical Engineering, University of Birmingham.

Amgwerd, and Preis,[3] who compared the effect of vanadium pentoxide and that of a natural fuel oil ash, containing 66·6 per cent V_2O_5, 12·8 per cent SO_3, and 8·7 per cent Na_2O, on a number of heat resisting steels over a wide range of temperature. It was found that at temperatures above their melting points both vanadium pentoxide and the ash corrode the alloys by destruction of the protective oxide films. Although vanadium pentoxide alone has a very marked effect, it was found that the alkali content influences the attack and enhances corrosion considerably with rise in temperature.

The problems of corrosion and deposition can be overcome in a number of ways. In the design of gas turbines, deposition might be prevented by gas cleaning or, alternatively, it has been suggested, by arranging for incomplete combustion of the oil droplets and thus coating the ash with carbon. Deposition alone might also be overcome by regular cleaning of the affected parts, or, alternatively, some additive might be found which inhibits corrosion and ash deposition. On the other hand, these problems are completely absent when distillate fuel are used, and consequently some method of removing ash-forming constituents by an operation cheaper than distillation would be attractive.

The immediate object of the present work was the isolation and identification, as far as possible, of the compound containing vanadium and other inorganic elements present in the fuel oils, in order to throw some light on the ultimate objective of designing a cheap process for their removal.

Treibs [4] was the first to suggest that vanadium was present in petroleum as an organic compound. Whilst studying the distribution of porphyrins of the chlorophyll and hæmin series in organic mineral substances, he isolated a vanadium porphyrin complex from an oil shale and, subsequently, similar complexes were identified spectroscopically in mineral oils by comparison with spectra of known vanadium porphyrin compounds.[4-7] Similarly, the presence of nickel and iron porphyrins has been suggested, but usually most of the iron is present as adventitious inorganic material. The occurrence of the porphyrins with vanadium and iron is a secondary phenomenon, according to Treibs, which depends on the well-known tendency of porphyrins to form complex compounds. The vanadium complexes are extraordinarily stable, and it is thought that less rigidly combined metals are displaced. This would account for the noticeable accumulation of the rare element, vanadium, in the ashes of petroleums and asphalts. Sodium compounds may be present as a mixture of adventitious inorganic compounds and as sodium salts of organic acids.

Analytical Procedure

Preliminary spectrochemical work on an Iraq oil showed the presence of traces of many elements such as aluminium, calcium, silicon, magnesium, copper, etc., but only sodium, iron, vanadium, and nickel were present in significant quantities. After considerable investigation, the following procedure was adopted for the quantitative determination of the four principal elements in the ash.

Determination of Ash Content

A weighed sample of oil is ignited in a platinum dish, allowed to burn, and the residue heated in a muffle furnace at 450° C until the ash is free from

carbonaceous matter. Chemical oxidation of a fraction using a nitric and sulphuric acid mixture showed that there is no measurable loss of vanadium on burning.

Determination of Vanadium, Nickel, and Iron

The ash is fused with sodium bisulphate, leached with water, and aliquot portions used separately to determine the elements.

(a) *Vanadium* (*Phosphotungstate Method*).—To the aliquot portion is added 5 ml concentrated nitric acid, 5 ml phosphoric acid (3 : 2). The solution is heated to boiling and 5 ml sodium tungstate solution (16·5 g in 100 ml water) added. After cooling and diluting to 100 ml, the drum reading on a Hilger " Spekker " photoelectric absorptiometer is obtained, using Ilford No. 601 filters (4300 Å) and the vanadium concentration read from calibrated curves previously prepared.

(b) *Nickel* (*Dimethylglyoxime Method*).—To the aliquot portion is added 2 ml hydrochloric acid (75 per cent). 5 ml ammonium citrate solution (25 per cent), 2 ml 0·025N iodine solution, 5 ml dimethylglyoxime solution (0·1 per cent in 50 per cent ammonia solution), and the solution diluted to 50 ml. The nickel concentration is found from a drum reading obtained using Ilford No. 604 filters (5200 Å).

(c) *Iron* (*Thiocyanate Method*).—To the aliquot portion is added 10 ml hydrochloric acid (75 per cent), 10 ml ammonium persulphate solution (0·5 per cent), the solution cooled to constant temperature, 10 ml potassium thiocyanate solution (20 per cent) added, and the solution diluted to 50 ml. The iron concentration is found from a drum reading obtained between 10 and 20 min after development of the colour, using Ilford No. 603 filters (4900 Å), the solution being exposed to light as little as possible.

Determination of Sodium

A separate sample of ash is treated with sulphuric acid and the sulphated ash heated in a Meker burner and leached with water. Sulphate, iron, etc., is then removed by precipitation, the filtrate concentrated, and the sodium precipitated and weighed as the zinc uranyl acetate salt.

Comparison of Residual Oils

Vanadium, nickel, and iron analyses were carried out on several residual oils obtained from Middle East crudes and on one from Venezuela. The

TABLE I

Oil residue	% Residue on crude	Ash, %		Vanadium, %		Nickel, %		Iron, %	
		On residue	On crude	On residue	On crude	On residue	On crude	On residue	On crude
Venezuelan	58	0·115	0·0666	0·0468	0·0272	0·00680	0·000394	0·00105	0·00061
Agha Jari (Iran)	45	0·0503	0·0226	0·00670	0·00302	0·00183	0·000821	0·00257	0·00116
Dammam	17·8	0·0148	0·00262	0·00227	0·000404	0·000638	0·000114	0·00157	0·00027
Abqaiq–Dammam	34	0·00908	0·00308	0·00101	0·000343	0·0000194	0·0000659	0·000483	0·00016
Abqaiq	17·5	0·0210	0·00367	0·00169	0·000296	0·000293	0·0000512	0·00341	0·00060
Qatar	32	0·00629	0·00201	0·00165	0·000528	0·000442	0·000141	0·000463	0·00015
Iraq A	32·5	0·0168	0·00547	0·00630	0·00205	0·00252	0·000819	0·000326	0·00011
Iraq B	45·8	0·0303	0·0139	0·00528	0·00242	0·00248	0·00114	0·00226	0·00104
Kuwait	61	0·0245	0·0149	0·00337	0·00205	0·000911	0·000557	0·0003	0·0002
Iran	42	0·0954	0·0401	0·00711	0·00299	0·00157	0·000658	0·00149	0·00062

results are given in Table I. There is vanadium in all the residues, although the percentages vary widely; the Venezuelan crude, however, has almost ten times as much vanadium as any from the Middle East. All the residues analysed contain nickel, and the ratio of vanadium to nickel for all the Middle East crudes lies between 2 and 6. Iron was found in all residues, but it was difficult to estimate how much of this is adventitious.

It appears that high asphaltene content is associated with high vanadium content of the oil (Table II), although there is no precise common relation-

TABLE II

Oil residue	Vanadium, % × 10^3	Specific gravity, 20° C	Sulphur, %	V/Ni	Hexane Insoluble, % (H.I.)	Asphaltene, % (A)	$\frac{H.I.}{V} \times 10^3$	$\frac{A}{V} \times 10^3$
Venezuelan	46·8	1·001	2·60	6·9	14·2	14·2	3·02	3·02
Iran	7·11	0·946	2·44	4·5	2·31	1·95	3·25	2·74
Agha Jari (Iran)	6·70	0·947	2·40	3·7	4·22	4·00	3·30	5·97
Iraq A	6·30	0·957	4·06	2·5	4·00	4·00	6·35	6·35
Iraq B	5·28	0·943	3·59	2·1	5·67	5·45	10·7	10·3
Kuwait	3·37	0·940	3·35	3·7	1·49	1·49	4·43	4·42
Dammam (Saudi Arabia)	2·27	0·982	3·50	3·6	6·18	5·61	27·2	24·8
Abqaiq (Saudi Arabia)	1·69	0·964	3·19	5·8	3·32	2·86	19·7	16·9
Qatar	1·65	0·958	3·92	3·7	3·44	3·44	20·8	20·8
Abqaiq–Dammam	1·01	0·940	2·65	5·2	1·41	1·12	14·0	11·1

N.B.—(1) All data reported are based on residues.
(2) H.I. obtained by precipitation using 10 ml hexane per 1 g residue.
(3) Asphaltene % is H.I. soluble in benzene.

ship in the ratio of asphaltenes to vanadium, which varies between 2×10^2 and 25×10^2. However, when the asphaltenes are precipitated, they do not contain all the vanadium.

IRAQ RESIDUE

This work was largely restricted to an Iraq residual fuel oil, and the following sections are concerned with work on one Iraq residual fuel oil or an asphalt obtained from the same oil by propane precipitation. The sodium compounds were conveniently removed by water extraction of the residue diluted with benzene and acetone, and were found to be almost entirely sodium sulphate and chloride. Iron was present as inorganic material, such as iron oxides, which was nearly all removed by filtration together with some silica. Very small fractions of the iron and sodium might have been in solution in the oil, but these were not investigated further. The remaining metals present in important quantities were vanadium and nickel, which were shown to be oil-soluble or oil-dispersible, and which are not removed by water-washing or filtration. Attention has been largely concentrated on these metals.

Solvent Extraction

In an attempt to find a selective solvent for vanadium compounds, batch extractions of the fuel oil were carried out, using several solvents having widely different properties. Benzaldehyde, pyridine, mixed cresols, and methyl aniline were completely miscible with the fuel oil at normal temperatures. Immiscible solvents examined were: aniline, acetic anhydride, acetic acid, acetone, benzyl alcohol, cellosolve, cellosolve acetate, chlorex, ethylene chlorhydrine, ethyl alcohol, ethyl formate, furfural, furfuryl

alcohol, methyl cellosolve, *o*-toluidine, water, hydrochloric acid (concentrated and dilute), ammonia, and caustic soda solutions. None of these solvents was particularly selective under the conditions used, but *o*-toluidine and chlorex appeared to be the best. The results show that :—

(1) The vanadium complex is not water-soluble, but is soluble or dispersible in the crude oil.

(2) Although vanadium porphyrins are reported to be soluble in ethyl alcohol, glacial acetic acid, and acetic anhydride by Treibs [4] and Glebovskaya and Vol'kenshteĭn,[6] these solvents extract only a small proportion of the vanadium present.

(3) Although organic solvents of widely different structure were used, none had exceptional solvent power for the vanadium compounds as compared with the asphaltenes.

(4) There is no simple relationship between vanadium extracted and the density, surface tension, viscosity, dielectric constant, or internal pressure of the solvent.

It is well known that no vanadium appears in the distillate fraction obtained from crude oils, but is always concentrated in the residue. It appeared probable, therefore, that most of the vanadium might be removed with asphalt. Propane-precipitated asphalt from the same oil was therefore examined, and was in fact found to contain virtually all the vanadium present in the original fuel oil, but at a much higher concentration, 0·018 per cent vanadium in asphalt, compared with 0·0053 per cent in the fuel oil.

Extractions of the asphalt were carried out using chlorex, *n*-butanol, glacial acetic acid, and acetic anhydride. A slight enrichment in vanadium compounds occurs with chlorex, but there are considerable practical difficulties. *n*-Butanol extracts some low molecular weight material but little vanadium, and is of little use for the concentration of vanadium compounds. Both acetic anhydride and glacial acetic acid dissolve very little of the asphalt, and again there is very little enrichment in vanadium content.

Fractional Precipitation

Further examination of the asphalt showed that 97·3 per cent of the vanadium, 99·2 per cent of the nickel, and 86 per cent of the iron originally in the fuel oil was precipitated with the asphalt. Fractional precipitation

TABLE III

Analysis of Individual Precipitates

Hexane/oil Ratio *	% Total component precipitated				Vanadium content, %
	Oil	Ash	Vanadium	Iron	
0·69 : 1	6·0	28	0	65	0
1·3 : 1	3·5	17	14·9	6	0·023
2·6 : 1	2·6	6	24·0	6	0·049
3·6 : 1	1·2	33	8·0	2	0·036
4·8 : 1	1·0	7	6·3	5	0·034
7·7 : 1	1·0	13	4·0	8	0·021

* Wt to wt of precipitant to oil.

of the asphalt from the fuel oil was therefore carried out, and the distribution of the ash-forming constituents followed during the process. Successive precipitations were carried out with known weight ratios of the following precipitants : petroleum fractions such as *n*-pentane, *n*-hexane, petroleum ether, white spirit, and ethyl ether. The results followed a general pattern, and those shown in Table III may be considered typical. The cumulative results are shown graphically in Fig 1.

The results show that the lower molecular weight hydrocarbons are more effective in enrichment of vanadium by the precipitation method and that ethyl ether is a much poorer precipitant than the lower hydrocarbons. The amount of vanadium in each fraction also depends on the ratio of precipitant to oil. Most of the iron is precipitated with the first fraction, as would be expected.

Below a certain ratio of precipitant to oil (1 : 1 for hexane) little, if any,

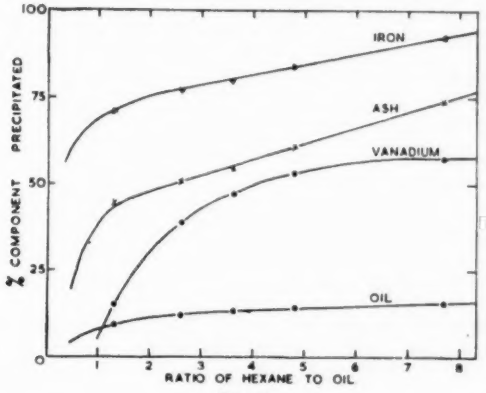


FIG 1

HEXANE PRECIPITATION OF FUEL OIL

vanadium appears in the precipitate. However, above this critical ratio, a relatively large proportion of vanadium is precipitated in a small amount of asphalt with only a small addition of precipitant, and for hexane the precipitated asphalt contains 0·049 per cent vanadium. After this first precipitation, the asphalt and vanadium precipitated falls off in successive precipitations. From asphalt–benzene solutions, it was found that the general distribution of the precipitated material is the same as for fuel oil, but the proportion of benzene present influences both the amount of asphalt and vanadium precipitated. The vanadium contents of the precipitates, however, are usually much higher, presumably because they contain less low molecular weight contaminants. These results are shown in Fig 2.

It might seem from the results that a Duosol type of countercurrent extraction, using a precipitant and a good solvent for the vanadium compounds, would be helpful. However, this was ruled out on practical grounds :—

(*a*) Choice of solvent was more or less limited to aniline, furfural or *o*-toluidine, as the solvent must be insoluble in the precipitant, hexane.

(*b*) *o*-Toluidine was miscible with a mixture of *n*-hexane and asphalt at normal temperatures.

(*c*) Neither furfural nor aniline dissolved sufficient asphalt for a countercurrent extraction to be satisfactory, even when benzene was added.

As the countercurrent extraction method for the enrichment of the vanadium compounds was found to be impracticable, the use of precipitants was further studied. It has been shown that a preliminary enrichment of

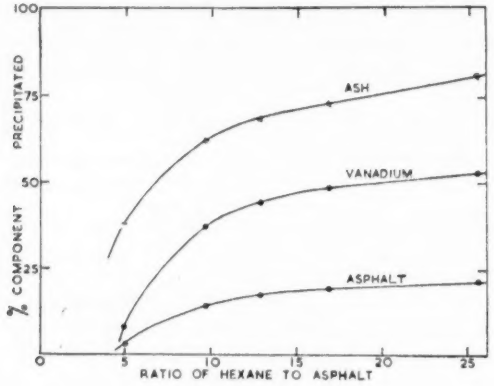


FIG 2

HEXANE PRECIPITATION OF ASPHALT FROM A 1 : 1 ASPHALT–BENZENE SOLUTION

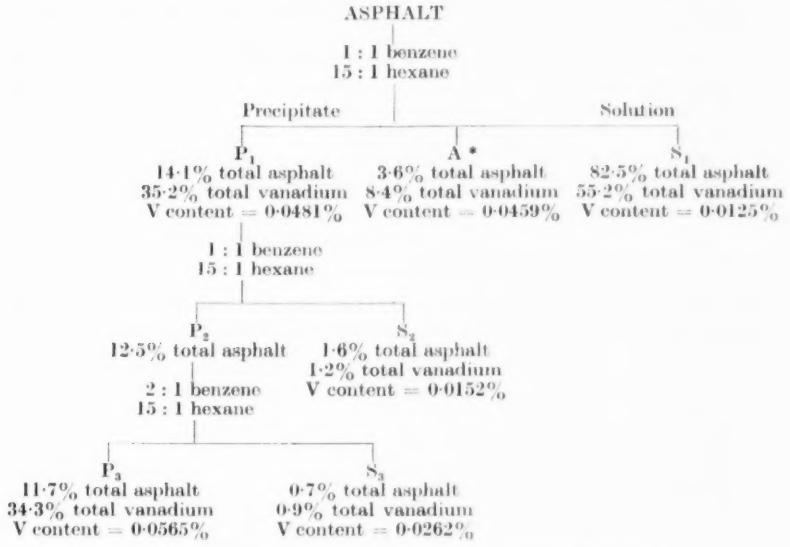
vanadium compounds is best obtained by precipitating asphalt from solution by the addition of low molecular weight paraffins. A systematic investigation was therefore made using a benzene solution of asphalt.

Precipitation of Asphalt

Propane-precipitated asphalt was dissolved in an equal weight of benzene, and *n*-hexane was added, so that a weight ratio of hexane to asphalt of 15 : 1 was obtained. The precipitate was then dissolved in benzene and precipitated again. A schematic outline of the procedure is shown in Fig 3, which shows also the vanadium contents of individual fractions. The amounts of these fractions and the vanadium obtained based on the total asphalt and vanadium are also shown. From these results, it appears that further precipitation of P_3 under the same conditions would increase the vanadium content only slightly, if at all. However, two attempts were made to concentrate the vanadium in fraction P_3 using (*a*) *n*-hexane and (*b*) mono-methyl aniline. A solution in excess benzene was partially precipitated by adding these compounds, but practically no further enrichment was obtained. It appears that a vanadium content of 0·065 per cent, or a little higher, is the maximum it is possible to obtain by fractional precipitation of the asphalt.

Although fraction S_1 contained as much as 55·2 per cent of the total vanadium, nevertheless, the concentration of vanadium was only 0·0125 per cent, and no further enrichment was achieved by fractional precipitation

using hexane. According to Knowles, Eckert, McCoy, and Weetman [8] precipitation with aniline separates petroleum resins into naphthenic and paraffinic fractions, but this treatment gave no significant redistribution of the vanadium in S_1. Extraction of S_1 with hot alcohol dissolved only 9·4 per cent and the extract contained 9·0 per cent of the total vanadium. In this connexion, it is of interest to note that the evidence of the presence of vanadium porphyrins has been obtained by spectroscopic observation in ethyl alcohol extracts of asphalt.



* Precipitate from hexane solution after removal of P_1.

FIG 3

PRECIPITATION OF ASPHALT

From all these results, it was concluded that further fractionation of P_3 and S_1 by solvent precipitation would not lead to a significant concentration of the vanadium, and attention was then turned to other methods.

Adsorption

Two experimental methods were used : (1) Soxhlet extraction of adsorbent–asphalt mixtures, a modification of adsorption methods used for the analysis of asphalt ; [9-11] (2) chromatographic adsorption using columns of activated alumina, followed by elution with a series of solvents of increasing polarity.

Results using the first method with various adsorbents such as fuller's earth, alumina, silica gel, calcium carbonate, talc, and carbon, may be summarized as follows :—

(1) No significant adsorption of " hard asphalt " was obtained which was not accompanied by a correspondingly large proportion of the vanadium.

(2) The best results were obtained for a chloroform extraction of a 4 : 1 alumina–asphalt mixture, after a preliminary extraction with aromatic-free petroleum ether. The chloroform extract contained 40 to 45 per cent of the total asphalt and 80 to 90 per cent of the total vanadium (vanadium content, 0·034 per cent). Some 5 per cent hard asphalt was not extracted, and the petroleum ether fraction contained about 50 per cent of the asphalt but with little vanadium, usually much less than 5 per cent of the total.

(3) No improvement was obtained by extraction with other solvent series, *e.g.*, pentane, *cyclo*hexane, toluene, chloroform, pyridine. All the extracts contained some vanadium, but there was very little in the pentane or petroleum ether fractions.

(4) Practically all of the vanadium from the original crude oil is concentrated in half the propane precipitated asphalt, *i.e.*, in 6·5 per cent of the crude oil.

(5) The ratio of vanadium to nickel remained approximately constant throughout the asphalt fractions.

Chromatographic adsorption of asphalt on an alumina column and development with petroleum ether, *cyclo*hexane, chloroform, and pyridine

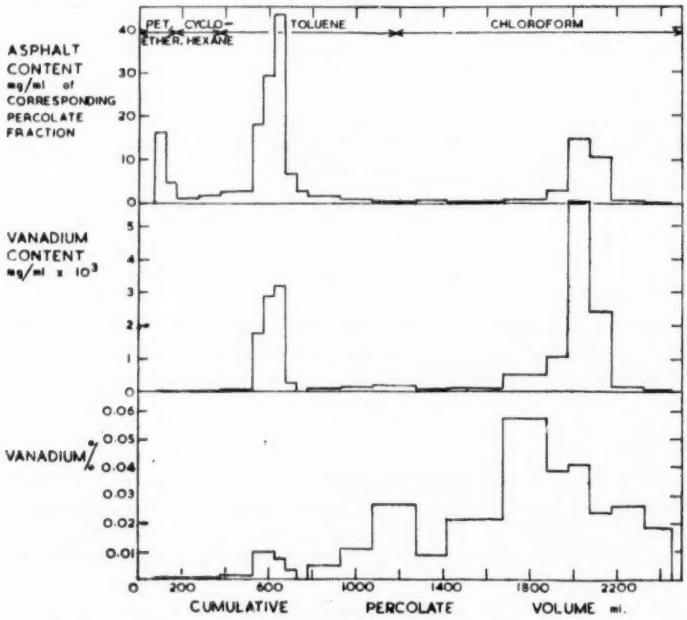


FIG 4

ADSORPTION FRACTIONATION OF ASPHALT

led to similar results. Practically no vanadium is extracted with petroleum ether and *cyclo*hexane; toluene extracts some, but the greatest concentration of vanadium compounds occurs in the chloroform fractions. This is shown in Fig 4.

Adsorption of Fraction S_1

The fraction S_1 mentioned above (Fig 3) was mixed with three times its weight of alumina and extracted with petroleum ether in a Soxhlet apparatus and a further extraction then made, using chloroform as solvent. This

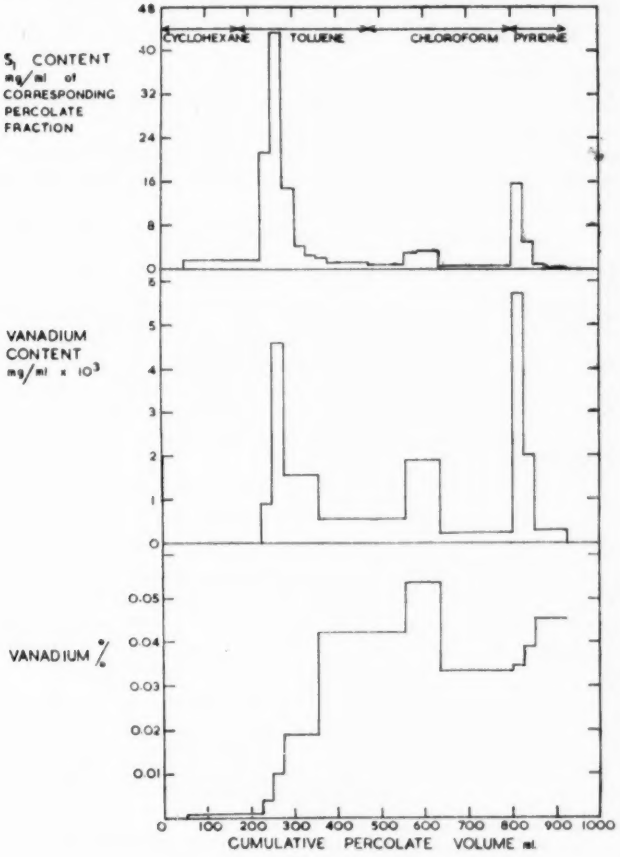


FIG 5

ADSORPTION FRACTIONATION OF ASPHALT FRACTION S_1

extract was isolated, dissolved in *cyclo*hexane, transferred to an alumina column, and chromatographic development carried out using *cyclo*hexane, toluene, chloroform, and pyridine as eluants. The results showed that 62 per cent S_1 can be extracted with petroleum ether, the extract containing

only 19 per cent of the total vanadium, and that by increasing the amount of adsorbent, the vanadium content of the extract would be lower.

After extraction with chloroform, 16 per cent of the fraction was still adsorbed. This is probably high molecular weight material not completely precipitated by hexane. The chloroform fraction itself was fractionated by chromatographic adsorption, and the results are represented in Fig 5. Sharp black bands were observed when eluting with toluene and pyridine. It is estimated that 75 per cent S_1, or 62 per cent asphalt, could be removed, accompanied by only a small percentage of the total vanadium. Thus, practically all of the vanadium, in the Iraq oil fuel is concentrated in the asphaltenes, representing 5 per cent of the crude oil.

Adsorption of Fraction P_3

Fraction P_3 (Fig 3) was very strongly adsorbed from a toluene solution, but chromatographic development was achieved using chloroform and finally pyridine. Two very sharp dark brown–black bands were obtained on elution, and are shown in Fig 6. Very little enrichment was obtained,

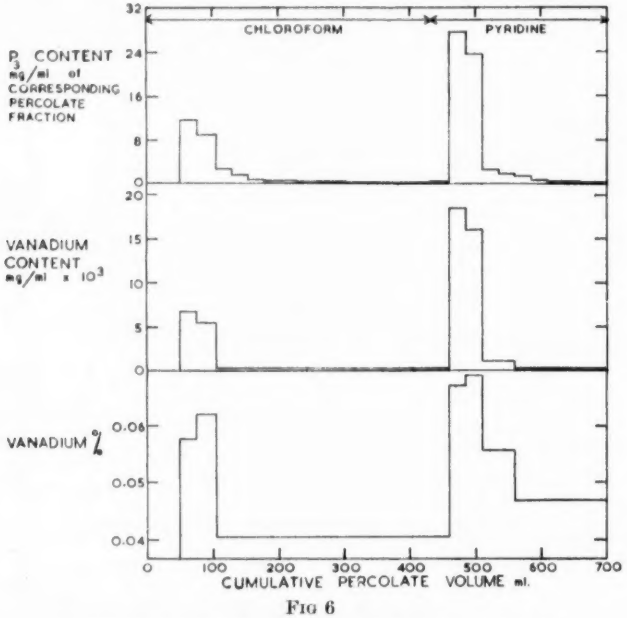


FIG 6

ADSORPTION FRACTIONATION OF ASPHALT FRACTION P_3

but results show that P_3 can be separated into at least two distinct fractions having about the same vanadium content, 0·060 per cent and 0·067 per cent. The first fraction contained 24·2 per cent of the P_3 fraction and 24·0 per cent of the total vanadium, the second contained 56·4 per cent of the P_3 fraction and 60 per cent of the total vanadium.

All these results have thus shown that although separation of asphalt

fractions containing vanadium compounds can be achieved, treatment of these gives hard asphalts having vanadium contents of the same order. It was decided, therefore, to investigate further splitting of the hard precipitate, using the Soxhlet extraction method, but employing different solvents and adsorbents.

(a) *Effect of Different Solvents*

Precipitates similar to P_2 or P_3 were mixed with alumina in the ratio of 1 : 15 and extracted with a series of solvents. Part of the precipitates was removed by the first solvent, *cyclo*hexane or carbon tetrachloride, and the extracts had relatively low vanadium and nickel contents. Other fractions, obtained by continued extraction with benzene, toluene, chloroform, acetone, pyridine, ethylene dichloride, ethylene chlorhydrin, chlorobenzene, etc., had all substantially the same vanadium and nickel contents, 0·058 to 0·069 per cent and 0·022 to 0·027 per cent respectively. Thus, no significant enrichment for either element was obtained by any solvent used. Furthermore, the ratio of vanadium to nickel is roughly constant for all fractions obtained. Thus, these elements both occur together either as similar complexes or in one molecule.

(b) *Effect of Different Adsorbents*

Using the above method with a series of different adsorbents (silica gel, fuller's earth, alumina, and calcium carbonate) and extracting first with carbon tetrachloride and then ethylene dichloride, the results obtained were very similar. The adsorbed fractions had the highest vanadium and nickel contents (calculated by difference), the vanadium contents being 0·060 $\pm$ 0·004 per cent and nickel contents 0·026 $\pm$ 0·001 per cent.

(c) *Effect of Different Adsorbent : Precipitate Ratios*

Reprecipitated asphalt was mixed with aluminium oxide and extracted in a Soxhlet apparatus, using carbon tetrachloride and then ethylene dichloride. The final fraction was not extracted, but its vanadium and nickel contents were calculated from the analyses of the extracts and of the original precipitate. Adsorption from both carbon tetrachloride and ethylene dichloride solutions appears to be maximum at a ratio of 25 parts adsorbent to 1 part precipitate; 68 per cent of the total precipitate was adsorbed from a carbon tetrachloride solution and 44 per cent from an ethylene dichloride solution. Once again, the final fractions had constant vanadium and nickel contents—V% = 0·069 $\pm$ 0·003, Ni% = 0·028 $\pm$ 0·001.

TABLE IV

Method	Vanadium, %	Nickel, %
Fractional precipitation . . .	0·065	—
Adsorption fractionation of P_3 . .	0·067	—
Soxhlet extraction :		
(1) different solvents (*a*) . . .	0·066	0·025
(2) different solvents (*b*) . . .	0·058	0·026
(3) different adsorbents . . .	0·060	0·026
(4) different adsorbent ratios . .	0·069	0·028

The vanadium and nickel contents of the final fractions, using the above methods (with different starting fractions), are summarized in Table IV. The highest vanadium content obtained was 0·074 per cent, and the highest nickel content 0·029 per cent.

Thus, with all these various methods, there is a limit to the enrichment of vanadium and nickel, and further treatment of concentrated fractions fails to yield material of higher vanadium concentration.

An examination of the analyses (Table V) of some of the fractions obtained

TABLE V

Analysis of Oil and Asphalt Fractions

No.	Fraction	V, % × 10^3	Ni, % × 10^3	V/Ni	Mol. wt *	C, %	H, %	C/H	S, %	N, %
1	Petroleum ether extract of an alumina–asphalt mixture	3·26	3·36	0·97	—	82·9	9·7	8·55	5·77	1·3
2	Ether soluble fuel oil	4·66	2·08	2·2	405	82·6	11·1	7·45	3·50	0·8
3	Fuel oil	5·28	2·48	2·1	420	82·5	11·2	7·35	3·59	1·0
4	Hexane soluble asphalt	14·3	6·83	2·1	700	82·0	9·25	8·85	6·9	1·2
5	Propane precipitated asphalt	18·0	8·61	2·1	855	81·6	9·01	9·1	7·25	1·3
6	Ether precipitated fuel oil	38·9	18·1	2·2	1200	80·5	8·45	9·5	8·44	1·9
7	Soluble fraction from re-precipitation of hexane precipitate (8)	53·2	22·3	2·4	1640	80·5	7·75	10·4	9·7	2·6
8	Hexane precipitated asphalt	60·0	26·6	2·3	1720	80·3	7·73	10·4	9·8	2·6
9	Precipitate from re-precipitation of hexane precipitate (8)	64·0	28·0	2·3	1790	80·0	7·70	10·4	9·6	2·7
10	Re-precipitated asphalt (P_1)	63·0	27·1	2·3	—	80·0	7·39	10·8	10·2	1·9
11	P_2 †	53·4	26·0	2·1	—	79·7	7·55	10·6	10·6	1·6
12	P_3 †	68·1	27·0	2·5	—	80·5	7·37	10·9	9·54	2·4
13	P_4 †	71·2	28·5	2·5	—	80·0	7·28	11·0	10·2	2·0

* Ebullioscopic molecular weights.

† P_2 obtained by Soxhlet extraction of a P_1–alumina mixture using carbon tetrachloride; P_3 by continued extraction, using ethylene dichloride; P_4 is the adsorbed fraction, results calculated from analyses of P_1, P_2, and P_3.

again shows that the concentration of nickel in the fractions is remarkably parallel to that of the vanadium, except for the first fraction. It also appears that there is a general tendency for higher vanadium and nickel contents to be associated with higher sulphur and nitrogen contents, C : H ratios, and molecular weights. It is of interest to compare the elemental analyses which Treibs [4] obtained for a crystalline vanadium porphyrin isolated from an oil shale and which he compared with known vanadium porphyrins : $C_{32}H_{34}N_4VO$ Calc C, 70·93; H, 6·33; V, 9·42; C : H, 11·2. $C_{32}H_{34}N_4V(OH)$ Calc C, 68·67; H, 6·49; V, 9·12; C : H, 10·6. Found C, 69·97; H, 6·30; V, 9·56; C : H, 11·1.

There is no similarity between these results and those obtained in the present work, which are given in Table V. Although the C : H ratio approaches that of a porphyrin in the fractions with higher vanadium concentrations, the latter would have to be increased one hundred times to give comparable figures. It may be that both vanadium and nickel are connected to a porphyrin structure, which is in turn part of a more complex compound.

Adsorption Spectra

Adsorption spectra were obtained for asphaltene–resin fractions having high vanadium contents in the wavelength range, 5000 Å to 7000 Å using a

Unicam photo-electric spectrophotometer. These were compared with similar spectra obtained by Glebovskaya and Vol'kenshteĭn [6] and Skinner.[7]

Adsorption maxima were obtained for an ether extract of an adsorbent precipitate mixture at 5680 Å and for an ordinary alcohol extract, at 5690 Å and 5330 Å. These agree quite well with figures given by Treibs [4, 5] and Stern and Deželić [12] for synthetic vanadium porphyrin complexes (Table VI). The coincidence of the absorption maxima at 5700 Å for oil extracts

TABLE VI

Absorption Spectra Maxima

Material	Maxima, Å	Reference
Vanadium salt of *meso*porphyrin IX dimethyl ester (in dioxane)	5700, 5330	Stern and Deželić [12]
Vanadium salt of *meso*porphyrin	5702, 5315	Treibs [5]
Petroleum and bituminous extracts	5750 to 5720	Treibs [5]
Alcohol extracts of Russian oils	5709, 5330, 4050	Glebovskaya and Vol'kenshteĭn [6]
Alcohol extracts of Santa Maria Valley crude	5700, 5310, 4070	Skinner [7]

and for the synthetic complexes is usually taken as evidence that vanadium in petroleum is present wholly as a vanadium porphyrin. For the precipitate examined, no absorption maxima could be observed when dissolved in toluene, and, although the ether and alcohol extracts showed maxima corresponding to a vanadium porphyrin, the red ether extract contained only 3·5 per cent of the total vanadium in the precipitate and the alcohol extract showing two less conspicuous maxima contained even less. No maxima corresponding to nickel porphyrins were observed, although the nickel content of the precipitate was relatively high.

Thus, although absorption spectra suggest that part of the vanadium may be present as a porphyrin complex, it would appear that only a very small proportion of the vanadium is present in this form. Most of the evidence reported in the literature for a vanadium porphyrin structure is based on absorption spectra of alcohol or ether extracts, which, for the Iraq oil at least, contain only a very small proportion of the total vanadium. It is possible that both vanadium and nickel are connected to a porphyrin nucleus, which is in turn part of a more complex molecule of high molecular weight. Other substituents attached to the porphyrin nucleus would explain slight differences in wavelength and complete masking of absorption maxima.

Distillation of the Asphalt

Vanadium compounds do not appear in the distillate fractions obtained from crude oils under normal conditions. It was thought possible that they might distil at sufficiently low pressures. However, molecular distillations carried out indicated that the vanadium compounds are not volatile below 300° C (bath temperature) at 10^{-5} mm Hg pressure, although approximately half the asphalt was distilled.

A cracked distillate obtained by heating asphalt at dull red heat also contained no vanadium. The residue was 38·5 per cent wt of the original

asphalt, and when treated with benzene only 3 per cent of the original vanadium was soluble. Thus, although comparatively stable to heat treatment, the vanadium compounds are transformed at red heat to insoluble compounds.

Concentration of Vanadium Compounds in a Venezuelan Residue

Since the Venezuelan residue had a very high vanadium content, 0·0468 per cent compared with 0·00528 per cent for the Iraq residual oil, it was used in an attempt to concentrate vanadium compounds using the methods outlined above. Soxhlet extraction of an alumina residue mixture using petroleum ether (boiling range, 40° to 60°C) showed that 64·6 per cent residue was extracted with only 1 per cent total vanadium. This is comparable with the results obtained for the Iraq asphalt. However, the chloroform and pyridine fractions had very high vanadium contents, 0·129 and 0·141 per cent respectively, which are far greater than the highest vanadium content obtained for any Iraq fraction (viz., 0·074 per cent). Successive precipitations and Soxhlet extractions showed that the vanadium content of the fractions could be increased, but again to only a limiting value, about 0·27 per cent. This is still far short of the analytical results of Treibs [4] for synthetic vanadium porphyrin complexes, all of which have vanadium contents between 9 and 10 per cent.

The results obtained show that the vanadium compounds are organic and concentrated in the asphalt portion of the Venezuelan oil. The vanadium is distributed throughout 35·4 per cent of the residue (20·5 per cent of the crude), and the fractions containing most vanadium are the least soluble asphaltene fractions with the highest C : H ratios and sulphur contents. Thus, there is a close similarity between the distribution of vanadium in Iraq and Venezuelan residues, although the latter contain much greater amounts of vanadium. It is significant that the Venezuelan crude also contains a much higher proportion of asphaltenes.

The Nature of the Ash-forming Constituents

The iron compounds present in petroleum can be removed together with silica by filtration : they are probably oxides whose presence is adventitious. The sodium compounds are principally chloride and sulphate, and these may be removed by washing with water, which may, of course, be a different operation in practice. The vanadium and nickel compounds are of particular interest. The present work indicates that they are present in compounds closely related with each other. This has been mentioned by previous workers.[13–15] Shirey, for example, has pointed out that high vanadium and nickel contents are usually associated with asphaltic base crudes. There is no doubt that vanadium porphyrins have been identified in petroleum.[4–7] In the Russian work and in that of Skinner, the porphyrins were identified in alcoholic extracts of the oils. However, no previous work has indicated the proportion of the total vanadium which dissolves in alcohol. From the present work, the indication is that only a small part (about 3 per cent) of the vanadium compounds dissolve in alcohol, but that the part which does dissolve has probably a porphyrin structure.

The conclusion of Skinner,[7] that all the vanadium in Santa Maria Valley crude oil is present as vanadium porphyrin complex, is not proven and is probably quite wrong. Treibs [4] also used acetic acid as well as alcohol to isolate vanadium porphyrins, but no measurable vanadium could be extracted from the Iraq residue by this acid.

Both vanadium and nickel appear to be associated with the same molecules which probably make up the hard asphaltenes. This fraction is the less soluble, high molecular weight material, with high sulphur and nitrogen content, representing about 5 per cent of the Iraq oil and about 20 per cent of the Venezuelan.

Conclusion

Very much more must be known of the chemistry of asphalt before the problems of identification of the vanadium and nickel compounds can be solved. The experimental evidence indicates that vanadium and nickel are combined in big molecules, apparently inseparable from a considerable fraction of the oil. In the case of the Iraq crude oil, this is about 5 per cent.

Neither adsorption nor liquid–liquid extraction methods, singly or in combination, appear to offer any likelihood of removing the bulk of the vanadium in a highly concentrated fraction, so that distillation or cracking may be the most suitable method for eliminating the vanadium content. On the other hand, the use of suitable additives in the combustion of fuel oil containing vanadium compounds may be a more suitable alternative for eliminating blade corrosion.

Acknowledgments

This work was undertaken at the request of the Admiralty, who provided scholarships for two of the authors, F. D. H. and R. E. P.

References

[1] Hughes, D. F., and Voysey, R. G. *J. Inst. Fuel*, 1949, **22**, 197.
[2] Lloyd, P., and Probert, R. P. *Proc. Instn mech. Engrs*, 1950, **163**, 206.
[3] Schlapfer, P., Amgwerd, P., and Preis, H. *Schweiz. Arch. angew. Wiss.*, 1949, **15** (10), 291.
[4] Treibs, A. *Liebigs Ann.*, 1935, **517**, 172.
[5] Treibs, A. *Angew. Chem.*, 1936, **49**, 682.
[6] Glebovskaya, E. A., and Vol'kenshtein, M. V. *J. gen. Chem., Moscow*, 1948, **18**, 1440.
[7] Skinner, D. A. Paper presented at a Symposium sponsored by the Division of Petroleum Chemistry of the American Chemical Society, April 1951.
[8] Knowles, E. C., Eckert, G. W., McCoy, F. C., and Weetman, B. Paper presented at a Symposium sponsored by the Division of Petroleum Chemistry of the American Chemical Society, March 1950.
[9] Garner, F. H. *J. Instn Petrol. Tech.*, 1921, **7**, 98.
[10] Marcusson, L. "Die naturlichen und kunstlichen Asphalte," 2nd Ed., 1931.
[11] Hubbard, R. L., and Stanfield, K. E. *Industr. Engng Chem. (Anal.)*, 1948, **20**, 460.
[12] Stern, A., and Deželić, M. *Z. Phys. Chem.*, 1937, A **180**, 131.
[13] Shirey, W. B. *Industr. Engng Chem. (Industr.)*, 1931, **23**, 1151.
[14] Gulyaeva, L. A. *C.R. Acad. Sci. U.R.S.S.*, 1945, **48**, 43.
[15] Fester, G. A., and Cruellas, J. *Rev. Fac. quim. ind. agr., Santa Fe*, 1940–1, **9–10**, 3.

STABILITY OF FUEL OIL–GAS OIL BLENDS

By D. G. Butlin * (Member)

Summary

Improvements are suggested in the technique originally devised by the author for predicting the compatibility of asphaltic fuel oil and gas oil components to ensure stable blends.[1]

Fresh experimental evidence shows that the flocculating power of test diluent mixtures used in the xylene equivalent test is not only dependent on aniline point, but that this flocculating power is reduced when the surface tension is high.

It is suggested that, by making allowance for surface tension, it is possible to improve the aniline-point criterion for predicting the compatibility of a gas oil with a fuel of known xylene equivalent.

The method for determinining the xylene equivalent has been improved by replacing the white spirit by either *iso*-octane or *n*-heptane and also by substantially reducing the duration of the test.

Introduction

It was recognized that the technique devised by the author [1] for the selection of compatible components of fuel oil–gas oil blends suffered from certain deficiencies. It had been found, for instance, that two gas oils of the same aniline point (120° F), when blended with a certain fuel oil in the same proportion, produced very different amounts of precipitated sludge. It was also concluded that the choice of white spirit for the determination of xylene equivalent was not entirely satisfactory, and the suggestion was made that it would be desirable to substitute a pure hydrocarbon such as *n*-heptane or *iso*-octane for the arbitrary paraffinic diluent, white spirit.

This addendum to the original paper presents the results of further investigation of both these points, and Appendix I describes an improved method for the determination of xylene equivalent.

Substitution of Pure Hydrocarbon for the White Spirit used in the Xylene Equivalent Test

Xylene equivalents have been determined for six fuel oils using the following range of pure hydrocarbons, *n*-hexane, *n*-heptane, *iso*-octane, *n*-cetane, in addition to the white spirit used for the earlier work.

Table I

Fuel Oil Ref 12

Test no.	Text mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
1	Xylene/*n*-hexane	58	22	23·2
2	,, /*iso*-octane	66	26	23·75
3	,, /*n*-heptane	62	31	24·3
4	,, /white spirit	59	43	25·6
5	,, /*n*-cetane	71	57	27·25

* The Shell Petroleum Co. Ltd.

The results of these determinations are given in Tables I to VI and, for reasons which will appear later, aniline points and surface tensions of the compatible test diluent mixtures by IP 2/47 and 90/44 respectively, have been tabulated with their xylene equivalents.

TABLE II
Fuel Oil Ref 13

Test no.	Text mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
6	Xylene/*n*-hexane	52	37	22·5
7	,, /*iso*-octane	60	42	23·2
8	,, /*n*-heptane	56	46	23·8
9	,, /white spirit	52	60	25·3
10	,, /*n*-cetane	66	72	27·2

TABLE III
Fuel Oil Ref 14

Test no.	Text mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
11	Xylene/*n*-hexane	32	80	20·75
12	,, /*iso*-octane	44	84	21·5
13	,, /*n*-heptane	36	91	22·25
14	,, /white spirit	29	108	24·5
15	,, /*n*-cetane	46	120	27·1

TABLE IV
Fuel Oil Ref 15

Test no.	Test mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
16	Xylene/*n*-hexane	33	79	20·9
17	,, /*iso*-octane	44	84	21·6
18	,, /*n*-heptane	38	88	22·3
19	,, /white spirit	32	102	24·6
20	,, /*n*-cetane	48	115	27·1

TABLE V
Fuel Oil Ref 16

Test no.	Test mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
21	Xylene/*n*-hexane	62	14	23·6
22	,, /*iso*-octane	68	18	24·0
23	,, /*n*-heptane	65	23	24·6
24	,, /white spirit	63	32	25·7
25	,, /*n*-cetane	74	47	27·3

TABLE VI
Fuel Oil Ref 17

Test no.	Test mixture	Xylene equivalent	Aniline point, ° F	Surface tension, dyne/cm
26	Xylene/*n*-hexane	33	78	20·9
27	,, /*iso*-octane	44	84	21·7
28	,, /*n*-heptane	38	88	22·3
29	,, /white spirit	29	108	24·5
30	,, /*n*-cetane	43	126	27·0

The choice of the paraffinic diluent may now be considered.

Cetane, by reason of its high molecular weight within the gas oil range, is attractive, but, because of its high melting point, it may be difficult to detect the end point of the test. The rate of evaporation of cetane is lower than that of xylene, so that there is danger of differential evaporation altering the composition of the test mixture during the drying of the spot in the last stage of the test.

At the other end of the molecular weight scale, *n*-hexane is rejected because it is probably less readily available than *n*-heptane or *iso*-octane. Of these latter two, both are available as primary reference fuels and although either could be used, *iso*-octane is preferred by the author because of the higher aniline point.

The detailed procedure for determining xylene equivalent appears in Appendix I. It will be observed to differ from the method originally published in two respects, viz.:—

(*a*) The replacement of the white spirit diluent by *iso*-octane.

N.B. A note is added that *n*-heptane may be used instead of *iso*-octane.

(*b*) Reduction of elapsed time from approximately 24 hours to 2 to 3 hours.

MODIFICATION OF ANILINE POINT CRITERION FOR COMPATIBILITY OF GAS OIL WITH FUEL OIL

In the previous work [1] it was suggested that, in addition to aniline point, the surface properties of a gas oil might be connected with its compatibility with fuel oil. The solvent capacity of a gas oil for asphaltenes plays a large part in determining the stability of fuel oil–gas oil blends, and this can be expressed by various physical constants of the gas oil such as aniline point. The aniline point alone is not always a complete criterion, however, and it has been found advisable to use a combination of this with surface tension, since it has been shown that two gas oils with the same aniline point may have different surface tensions. The surface tension and aniline point of various diluent mixtures and their components were therefore measured. An endeavour was then made to establish an empirical relationship between these properties under the conditions of the xylene-equivalent test as determined with pure hydrocarbons and the white spirit diluent.

The basic data appear in Tables VII and VIII, and from these data curves

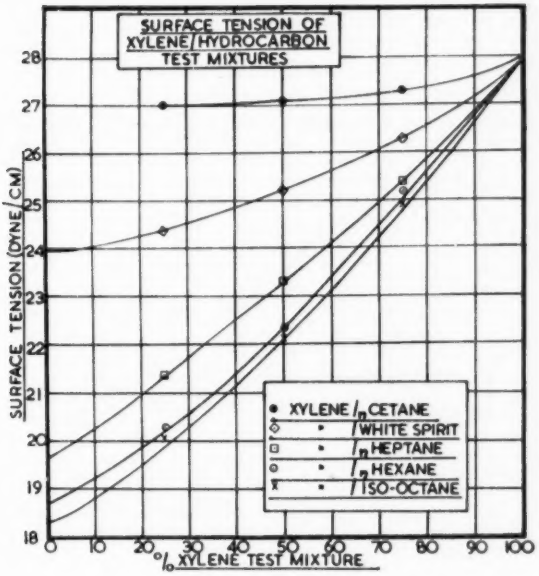

SURFACE TENSION OF XYLENE/HYDROCARBON TEST MIXTURES
SURFACE TENSION (DYNE/CM)
% XYLENE TEST MIXTURE
XYLENE/n CETANE
XYLENE/WHITE SPIRIT
XYLENE/n HEPTANE
XYLENE/n HEXANE
XYLENE/ISO-OCTANE

FIG 1

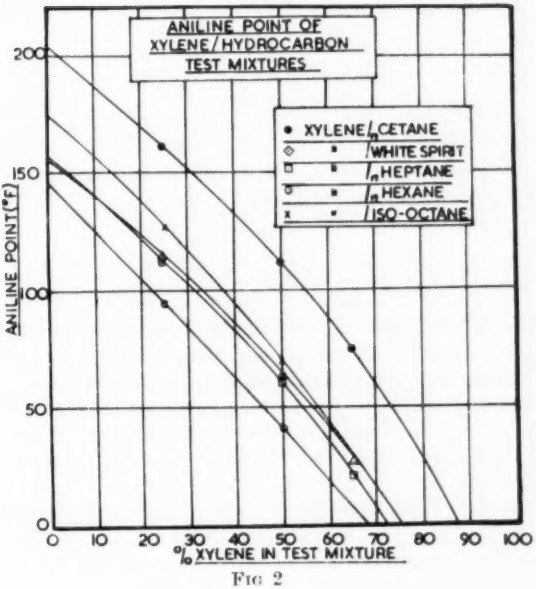

ANILINE POINT OF XYLENE/HYDROCARBON TEST MIXTURES
ANILINE POINT (°F)
% XYLENE IN TEST MIXTURE
XYLENE/n CETANE
XYLENE/WHITE SPIRIT
XYLENE/n HEPTANE
XYLENE/n HEXANE
XYLENE/ISO-OCTANE

FIG 2

were constructed so that the surface tension and aniline point of test diluent mixtures could be read off as required (Figs 1 and 2).

TABLE VII

Components of xylene equivalent text mixture	Aniline point, °F	Surface tension, dyne/cm, at 25° C
Xylene	—	28·0
n-Hexane	145	18·7
n-Heptane	157	19·6
iso-Octane	176	18·3
n-Cetane	204	27·0
White spirit	156	24·0

TABLE VIII

Xylene–hydrocarbon mixture	Aniline point, °F	Surface tension, dyne/cm, at 25° C
Xylene plus :		
25% vol *n*-hexane	—	25·2
50% ,, ,,	41	22·3
75% ,, ,,	94·5	20·3
25% vol *n*-heptane	—	25·4
35% ,, ,,	21	—
50% ,, ,,	61	23·3
75% ,, ,,	113	21·4
25% vol *iso*-octane	−6	24·9
35% ,, ,,	28	—
50% ,, ,,	69	22·1
75% ,, ,,	126·5	20·1
25% vol *n*-cetane	—	27·3
35% ,, ,,	75	—
50% ,, ,,	112	27·1
75% ,, ,,	161	27·0
25% vol white spirit	−1	26·3
35% ,, ,, ,,	27	—
50% ,, ,, ,,	64	25·2
75% ,, ,, ,,	114	24·4

Irrespective of the nature of the paraffinic diluent used with xylene, it follows from the definition of xylene equivalent that at the xylene-equivalent point all test diluent mixtures have equal flocculating power.

The next step, therefore, was to plot the surface tension against the aniline point of the test diluent mixtures corresponding to the xylene equivalents of each of six fuel oils (Tables I to VI) and to observe the relationship, if any, of these properties.

It was found that, for a given fuel oil, the points derived from test diluent mixtures of xylene and pure hydrocarbons lay on a straight line, and that the corresponding point with xylene and the white spirit diluent fell very nearly on this line.

The relationship surface tension/aniline point of test diluent mixtures at

the xylene-equivalent point for the six fuels under consideration is given in Fig 3.

It appears from the curves in Fig 3 that a given fuel oil will produce a stable blend with a series of test diluent mixtures, and that the fuel will tolerate a test diluent of increasing aniline point, provided the surface tension of the diluent increases proportionately.

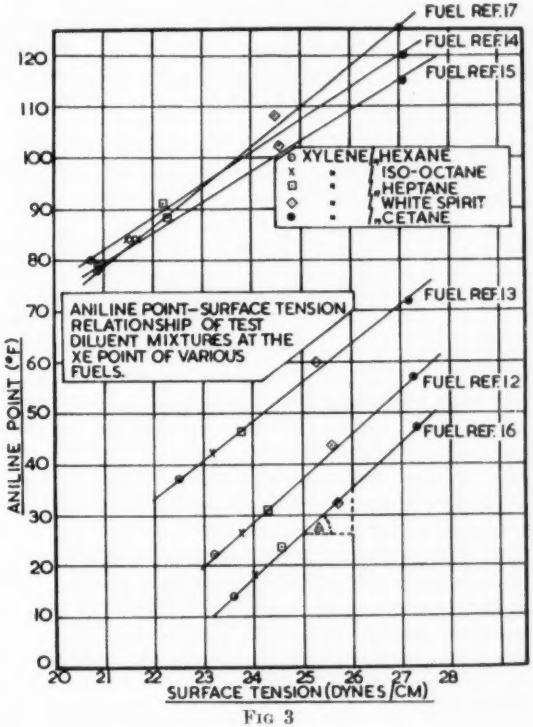


FIG 3

The relationship is illustrated by the slope, Δ, of the curves to the horizontal axis, and is shown in Table IX, where Δ expresses the difference in aniline point (° F) which can be tolerated in relation to a difference in

TABLE IX

Fuel oil Ref	Δ
12	8·8
13	7·5
14	6·4
15	6·0
16	9·0
17	8·0
Mean value	7·6

surface tension of 1 dyne. It will be noticed that Δ value ranges from 6·0 to 9·0 and that the average value for the six particular fuels examined is 7·6.

Application of Empirical Relationship between Aniline Point and Surface Tension of Test Diluent Mixtures to Blends of Gas Oil and Fuel Oil

It is mentioned above that two gas oils of the same aniline point, when blended with a fuel oil, produced widely different amounts of precipitated sludge, and that the surface tensions of these gas oils were found to be different. The details are shown in Table X.

Table X

Blend of 1 part Fuel Oil Ref 6 with 5 parts Gas Oil

Gas oil Ref	Aniline point, ° F	Surface tension, dyne/cm, at 25° C	Sludge, % wt after storage for 20 days
15	120	30·1	0·65
16	120	27·4	2·75

It will be seen that the gas oil having the surface tension of 30·1 dynes produces considerably less sludge than the gas oil having a surface tension of 27·4 or, in other words, gas oil 15 behaves as if its aniline point were considerably lower than that of gas oil 16.

Practical difficulties are encountered when attempts are made to extend the work described above by including gas oils in the range of test diluents, but the author suggests that his original criterion for stability of fuel oil–gas oil mixtures can be improved by assuming that the relationship which has been found for some pure solvents also holds for gas oils. Partial support is given to this idea by the way the white spirit diluent (a mixture of hydrocarbons but free from aromatics) fits into the picture.

As a first step to testing the usefulness of the assumption, blending stability curves have been made relating xylene equivalent to aniline point and surface tension of the test diluent mixtures. Curves for both *iso*-octane and *n*-heptane are shown in Fig 4.

An example can now be given showing how the experimental blending of a particular fuel was considered :—

Fuel Oil Ref 15
xylene equivalent (*iso*-octane) = 44

From the blending curve for xylene equivalent with *iso*-octane, it was found that this fuel is just compatible with a test diluent mixture having an aniline point of 84° F and surface tension 21·6 dynes. It was next assumed that the fuel will be compatible with a gas oil having an aniline point above 84° F if the surface tension of the gas oil is sufficiently greater than 21·6 dynes. A series of six gas oils was chosen, and the maximum permissible aniline point of each was calculated, allowing 6° F for every 1 dyne by which the surface tension of the gas oil was found to be greater than 21·6. In the cases where the maximum permissible aniline point was found to be

higher than the actual aniline point of the gas oil, it is predicted that the blend will be stable.

Actual blends of fuel oil with the six gas oils under consideration were made to the same dilution ratio (1 : 5), and the amount of sludge produced

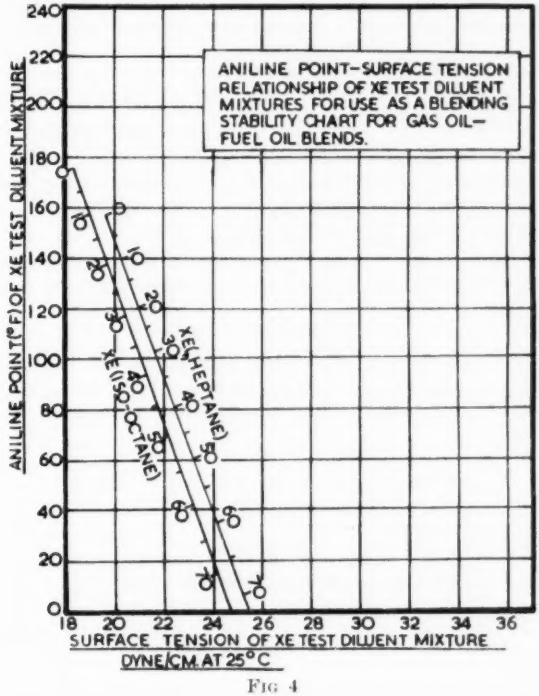


FIG 4

was determined by centrifuge after seven days storage at 100° F. The predicted and actual behaviours of fuel Ref 15, when blended with the six gas oils, are given in Table XI.

TABLE XI

Compatibility of Fuel Ref 15 *with Gas Oils Ref* 28 *to* 33

Gas oil Ref	Aniline point, ° F	Surface tension, at 25° C dyne/cm,	Maximum permissible aniline point, ° F	Predicted compatibility	Actual compatibility centrifuge sludge, % wt, after 7 days at 100° F
28	101	30·6	138	Compatible	0·05
29	112	28·8	127	,,	0·05
30	115	27·7	121	,,	0·10
31	156	26·7	115	Incompatible	1·40
32	161	28·2	124	,,	0·87
33	161	27·1	117	,,	1·30

The examples cited in Table XI show excellent correlation between predicted and actual compatibility, but it is not claimed that this striking example is sufficient to establish the validity of the argument beyond doubt. The evidence obtained from the behaviour of pure hydrocarbons under the conditions of the xylene equivalent test is so convincing, however, that it is considered justified to present the results at this stage.

Conclusions

(1) The flocculating power of a diluent for asphaltic fuel oil under the conditions of the xylene equivalent test decreases as the aniline point decreases, or as the surface tension increases.

(2) The combination of aniline point and surface tension is suggested as an improved criterion for predicting the compatibility of a gas oil with asphaltic fuel of known xylene equivalent.

(3) Either *iso*-octane or *n*-heptane may be used, in preference to the former white spirit diluent, in the determination of xylene equivalent.

Acknowledgments

The author is indebted to The Shell Petroleum Co. Ltd. for permission to publish the results of this investigation and also to colleagues in Shell Central Laboratories for assistance in preparing the paper.

Reference

[1] Butlin, D. G. *J. Inst. Petrol.*, 1950, **36**, 43.

Appendix I

Xylene Equivalent

Reagents

(a) iso-*Octane*.—Primary Engine Reference Fuel Grade. For specification see IP 42.

or

(b) n-*Heptane*.—Conforming to IP Specification (this is identical to Primary Engine Reference Fuel Grade).

(c) *Xylene*.—Conforming to NBA Specification No. 9, 1950 for 2° xylole, or to ASTM Specification D843, or equivalent.

Apparatus

25-ml conical flasks fitted with corks carrying air condensers in the form of glass tubes 400 mm long, 6 to 7 mm internal dia.

Procedure

Prepare a series of mixtures of xylene and *iso*-octane (see Note 1) containing from 5 to 95% v/v xylene, successive mixtures containing increments of 5% xylene. Filter the fuel oil through No. 40 Whatman filter-paper, if necessary in an oven at 95° to 100° C. This is to remove existing solids which might confuse the end point. Weigh $2 \pm 0{\cdot}02$ g of fuel into each of three 25-ml conical flasks. Choose three diluent mixtures to include the expected xylene equivalent and mixtures containing 5 per cent more and less respectively of the anticipated xylene equivalent. Add 10 ml of diluent mixture to each flask. Close each flask with a cork carrying the reflux condenser. Immerse the flasks up to their necks in a water-bath at 95° to 100° C and, when the contents are warmed, swirl each flask until the contents are homogeneous. Leave the flasks in the bath (maintained at 95° to 100° C) for 30 min, remove from the bath and store in the dark at room temp for 2 hr (min).

Swirl the contents of each flask and, with the aid of a 1-ml pipette, place one drop on to a No. 50 Whatman filter-paper supported by its edges and allow the stain to dry.

A black ring may or may not be visible in the stain. The xylene equivalent is given by the xylene content of the first diluent which fails to produce a ring. If all the stains show rings, further tests with diluents containing more xylene are carried out until the mixture is found which gives a clear stain. If all stains are clear, further tests are carried out with less xylene until a ring is produced. Then the xylene equivalent will be the xylene content of the last diluent to give a clear stain.

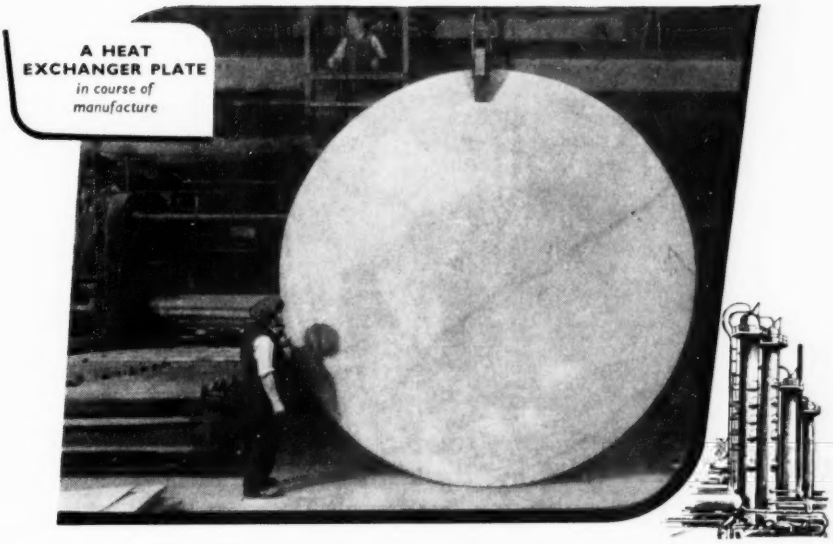
Reporting

Report the xylene equivalent as, for example, 26 to 30 per cent, which will indicate that a mixture containing 25 per cent xylene produced a ring but one containing 30 per cent did not. Report the dilution ratio at which the determination is made.

Note 1 : *n*-heptane may be used instead of *iso*-octane, in which case the xylene/*n*-heptane curve (Fig 4) is used for assessing compatibility.

Note 2 : In the examination of a waxy fuel, warm the test mixture to 50° C before making the spot test.

Note 3 : If greater accuracy is required, further tests may be carried out, as results will indicate, with diluents differing in xylene content by 1 per cent. However, for the purpose of compatibility assessment determination to within a bracket of 5 per cent suffices.



A HEAT EXCHANGER PLATE *in course of manufacture*

Tubes and Plates for Heat Exchangers

Birmingham Battery "True to Specification" products in non-ferrous metals are widely used in the Oil Industry.

"BATTERY" CONDENSER PLATES

in Naval Brass or Yellow Metal are produced up to the heaviest sizes required by the Oil Refineries.

CONDENSER TUBES

for Heat Exchangers, Steam Condensers, Oil Coolers etc., to British Standard and A.S.T.M. Specifications in—"BATALBRA" (76/22/2 Aluminium Brass), Admiralty Mixture (70/29/1 Brass), 70/30 Brass, Cupro-Nickel and Aluminium Bronze.

● Other "BATTERY" manufactures of interest to the Oil Industry are TUBES (up to 24" dia.), SHEETS, STRIP, ROD and WIRE in COPPER, BRASS, PHOSPHOR-BRONZE etc., to the latest British Standard Specifications. Where necessary, we should be pleased to work to customers' own requirements.

CONTRACTORS TO H.M. GOVERNMENT AND LEADING OIL COMPANIES

The BIRMINGHAM BATTERY and METAL CO LTD

SELLY OAK BIRMINGHAM 29

Over a Century of Independent Enterprise

A QUESTION OF PRECISION

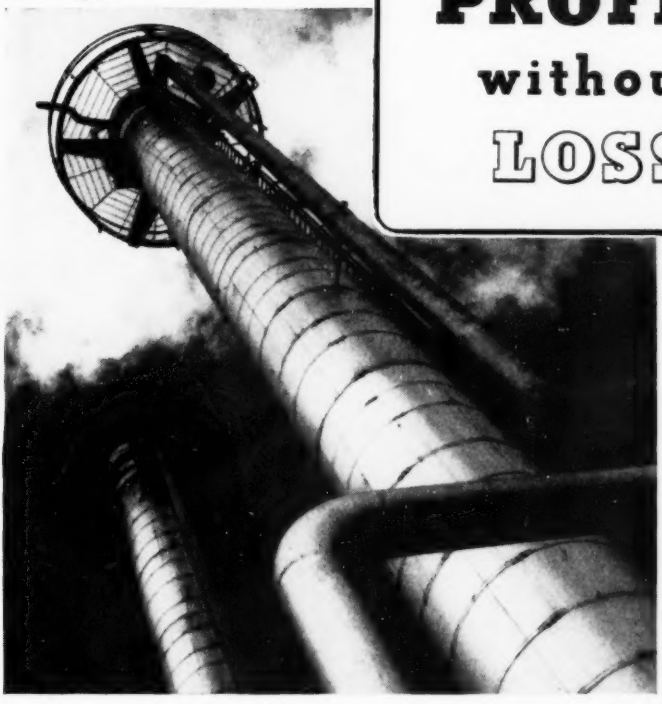
Attainment of perfect precision in execution is a long, hard road. The end brings success in proportion to the effort made. Like most elementary statements these are true. The world-wide success of Hayward Tyler — Byron Jackson Process Pumps for the Oil Industry is not fortuitous: it is the result of long and careful study and the correct application of the knowledge thus attained.

HAYWARD TYLER • BYRON JACKSON

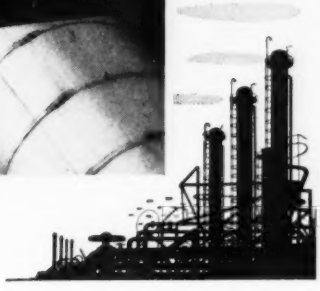
Precision Pumps for the Oil Industry

HAYWARD TYLER & CO. LTD · LUTON · BEDFORDSHIRE
PHONE LUTON 3951

A Shell Photograph



PROFIT without LOSS



KENYON
Planned HEAT INSULATION

Kenyon provide a *complete* thermal insulation service to the oil industry, including technical advice on thermal insulation specifications, and finishes for all conditions. Supply of materials, application, supervision, on sites throughout the world.
The photograph shows Fractionating equipment on Distillation units at Shell Chemical Plant, Stanlow, Cheshire, England.

Call in KENYON to keep the heat in

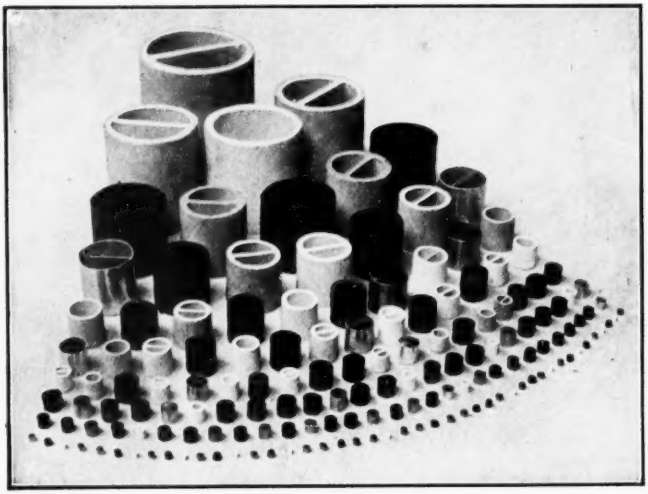
WILLIAM KENYON & SONS LIMITED

DUKINFIELD *Telephone:* ASHTON 1614/7 (4 Lines) CHESHIRE

KH 134

TOWER PACKINGS

LESSING AND PLAIN CONTACT RINGS FOR ALL PURPOSES



THE HYDRONYL SYNDICATE LTD.

14 GLOUCESTER ROAD, LONDON, S.W.7

Telephone: WEStern 4744 *Telegrams: HYDRONYL · KENS · LONDON*

LIST OF ADVERTISERS

	PAGE
Babcock & Wilcox, Ltd.	xv
E. B. Badger & Sons Ltd.	ix
Baird & Tatlock (London) Ltd.	Apr.
Baker Oil Tools, Inc.	Apr.
Birmingham Battery & Metal Co. Ltd. ...	i
British Oilfields Equipment Co. Ltd. ...	Apr.
Peter Brotherhood Ltd.	xi
W. P. Butterfield, Ltd.	Mar.
W. H. Capper & Co. Ltd.	xiii
Consolidated Pneumatic Tool Co. Ltd. ...	Apr.
A. F. Craig & Co. Ltd.	x
Crosby Valve & Engineering Co. Ltd. ...	Apr.
Cyanamid Products Ltd.	—
Dorman & Smith Ltd.	Apr.
English Drilling Equipment Co. Ltd. ...	xviii
Exactor Ltd.	Jan.
Foxboro-Yoxall, Ltd.	xvii
W. J. Fraser & Co. Ltd.	xx
Matthew Hall & Co. Ltd.	xvi
Hayward Tyler & Co. Ltd....	ii
H.M. Continuous Plant Ltd.	vii
Hydronyl Syndicate, Ltd.	iv
Wm. Kenyon & Sons, Ltd.	iii
Richard Klinger, Ltd.	Mar.

	PAGE
Lake & Elliott, Ltd.	Mar.
Lincoln Electric Co. Ltd.	vi
A. & J. Main & Co. Ltd.	v
May & Baker Ltd. (Lab. Chemicals) ...	Mar.
Metal Propellers, Ltd.	xix
Metropolitan-Vickers Electrical Co. Ltd.	Mar.
A. P. Newall & Co. Ltd.	Back Cover
Newman, Hender & Co. Ltd.	viii
Newton, Chambers & Co. Ltd.	Feb.
Nicerol, Ltd.	Apr.
Oil Well Supply Co.	Mar.
Samuel Osborn & Co. Ltd.	xiv
Oxford University Press	Apr.
Pulsometer Engineering Co. Ltd. ...	vii
Pyrene Co. Ltd.	Inside back cover
Quasi-Arc Co. Ltd.	Apr.
Sigmund Pumps Ltd.	Apr.
Tylors of London, Ltd.	Apr.
Wheesoe, Ltd.	Mar.
Henry Wiggin & Co. Ltd.	Apr.
John Wilkes, Sons & Mapplebeck Ltd. ...	Apr.
W. Martin Winn, Ltd.	Mar.
Yorkshire Copper Works, Ltd.	Apr.

STRUCTURES IN STEEL

We Specialise in

ALL TYPES OF STRUCTURES

required for

Oil Production and Refining.

ALSO

'KELVIN' *all iron* **and 'MAINSTEEL' PALISADING**

and All Types of FENCING

for HOME and OVERSEAS.

A. & J. MAIN & CO., LIMITED

LONDON : VINCENT HOUSE, VINCENT SQUARE, S.W.1

Telephones : Victoria 8375/6/7/8 *Telegrams :* Kelvin Sowest, London

WORKS AND REGISTERED OFFICE

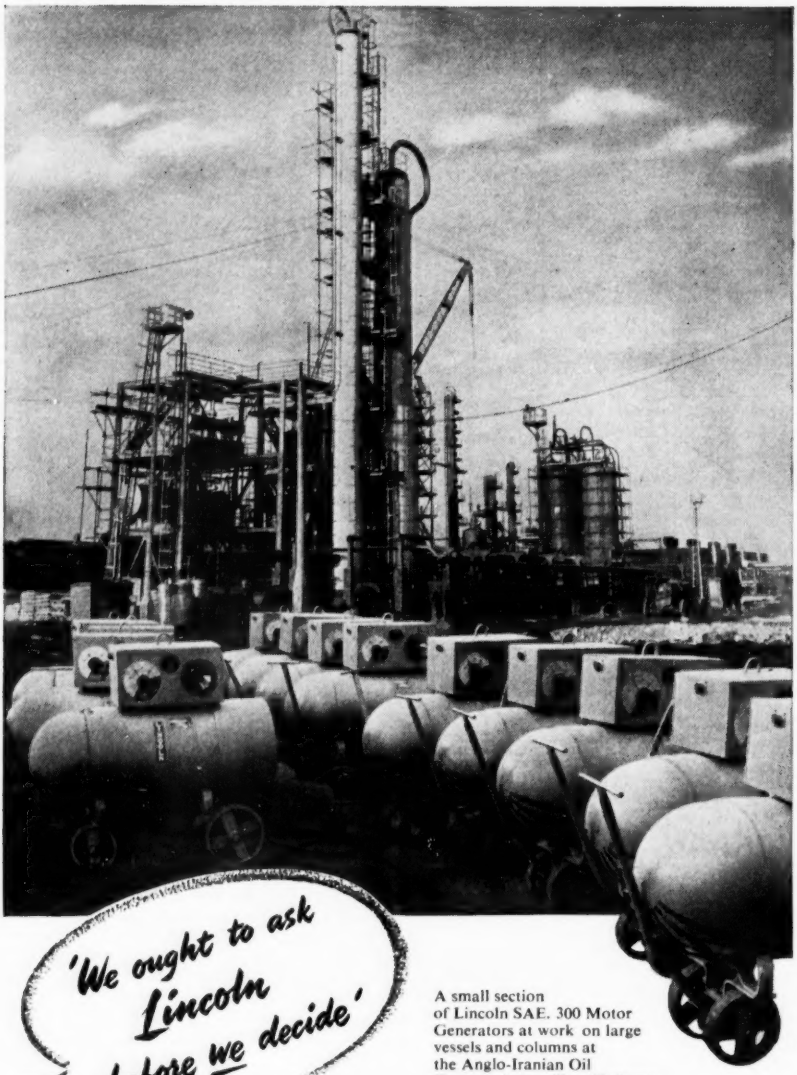
CLYDESDALE IRONWORKS, POSSILPARK, GLASGOW, C.2

Telephone: Possil 8381 *Telegrams:* Kelvin, Glasgow

CALCUTTA : Post Box 36, 16 NETAJI SUBHAS ROAD

also NAIROBI and CHITTAGONG

Kindly mention this Journal when communicating with Advertisers



A small section of Lincoln SAE. 300 Motor Generators at work on large vessels and columns at the Anglo-Iranian Oil Company's new Kent Refinery on the Isle of Grain, Kent. Lincoln welders and electrodes are playing an important part in this major development.

World's largest manufacturers of arc-welding equipment and electrodes

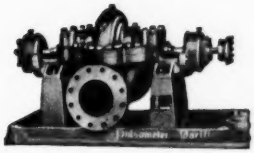
LINCOLN

LINCOLN ELECTRIC CO LTD · WELWYN GARDEN CITY · HERTS · WELWYN GARDEN 920

SMS9

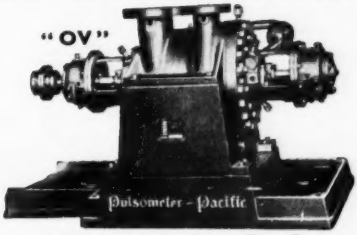
Pulsometer-Pacific

PUMPS FOR THE OIL INDUSTRY



"KH"

Horizontally Split Casing Single-Stage Hot Oil Pumps.



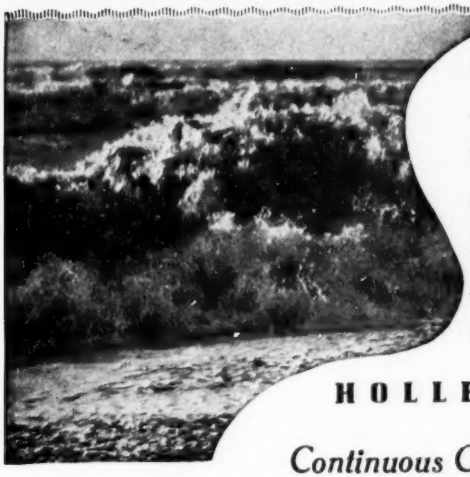
Vertically Split Casing Two-Stage And Three-Stage Hot Oil Pumps.

The above are some only of the designs included.

Established 1875 Advertisement No. 3316

Pulsometer Engineering C°. L^td^.,
Nine Elms Ironworks, Reading.
ENGLAND

CONTINUOUS WASHING



Holley Mott Plants are efficiently and continuously washing millions of gallons of Petroleum products daily Designed for any capacity. May we submit schemes to suit your needs?

HOLLEY (HM) MOTT

Continuous Counter-Current Plant

Telegrams:
"Typhagitor, Fen, London."
Telephone: Royal 7371/2.

World-Wide Licensees, **H.M. CONTINUOUS PLANT L^TD^.**
FOUR LLOYDS AVENUE, LONDON, E.C.3.

NEWMAN-McEVOY VALVES

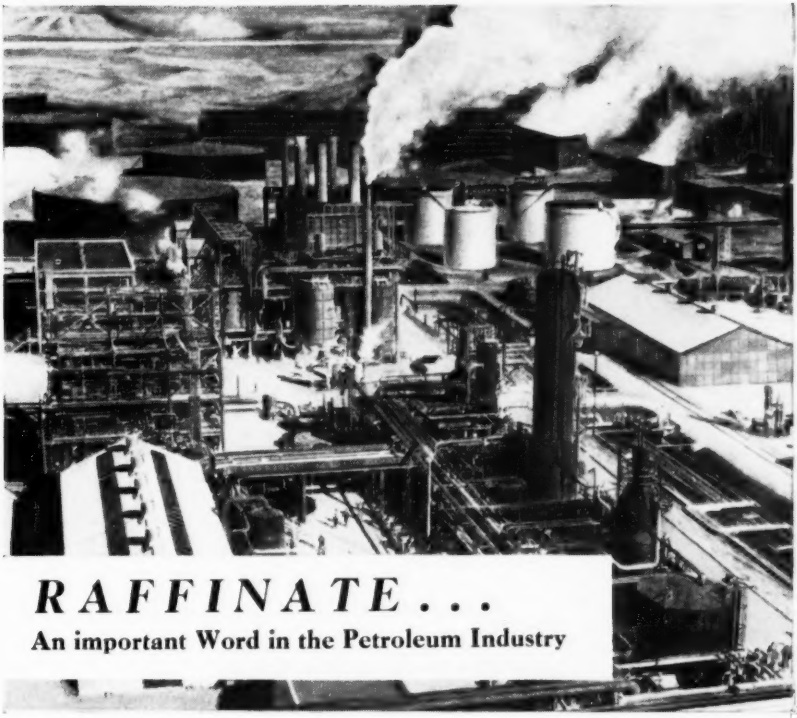
GIVE EFFICIENT DEPENDABLE SERVICE

These Valves have no equal for Christmas Tree and Flow Line service and are available in all sizes and for all working pressures normally required by the Oil Industry.

AUTOMATIC LUBRICATION CONDUIT GATE VALVE

Newman, Hender & Co. Ltd

WOODCHESTER GLOS. ENGLAND



RAFFINATE . . .

An important Word in the Petroleum Industry

Catalytic cycle stocks, when extracted with SO_2, often give high yields of raffinates of a quality equal or superior to that of the virgin charge. These products may then be blended into premium diesel or similar fuels or reprocessed in the cat cracker with minimum coke.

The SO_2 Extraction unit of the Phillips Petroleum Company at Phillips, Texas, shown in foreground above, is the second SO_2 plant to treat cat cycle stocks. Both plants were designed and built by Badger.

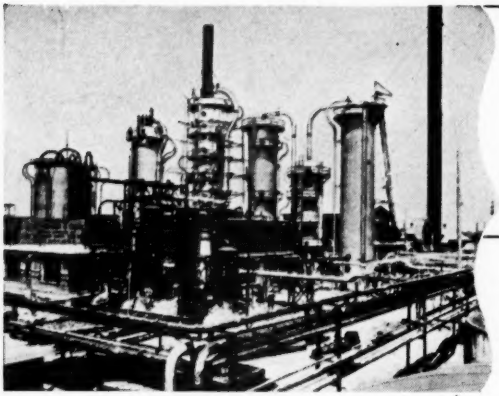
E. B. BADGER & SONS LIMITED

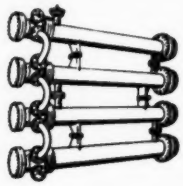
(Affiliated with Stone & Webster Engineering Corporation, Badger Process Division, U.S.A.)

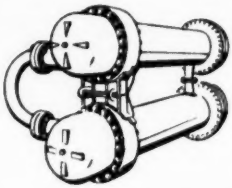
99 ALDWYCH, LONDON, W.C.2

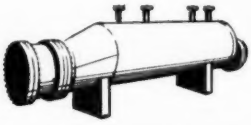
Process Engineers and Constructors for the Petroleum, Chemical and Petro-Chemical Industries.

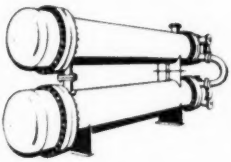
Kindly mention this Journal when communicating with Advertisers

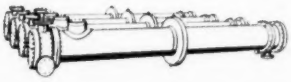












The CRAIG

COMPREHENSIVE SERVICE

Complete Refinery Design and Construction.

Atmospheric & Vacuum Distillation Units.

Combined Distillation, Cracking, Reforming and Vapour Phase Treating Units.

Pressure Distillate Re-run, Gasoline Recovery & Stabilisation Units.

Fractionating Columns and Tube Stills.

All types of Heat Exchange Equipment.

A. F. CRAIG & COMPANY LIMITED

CALEDONIA ENGINEERING WORKS

PAISLEY SCOTLAND

London Office: 727, Salisbury House, London Wall, E.C.2. *Telephone*: MONARCH 4756

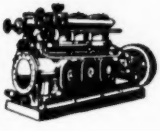
BROTHERHOOD
STEAM TURBINES

FOR DRIVING PUMPS, Etc.
Wide range—All types. Over 40 years' experience.
Hundreds in hand—thousands in service.

BROTHERHOOD
STEAM ENGINES
High speed Vertical up to 500 B.H.P.
Over one hundred in hand.

BROTHERHOOD
COMPRESSORS
Air, Gas and Refrigerating.

The widest range in the British Empire —made to suit your requirements.
Thousands in service.



BROTHERHOOD
REFRIGERATING PLANT
Ammonia, CO_2, Freon, SO_2, Methyl Chloride. Wide range—single and double acting—one or more stages.

BROTHERHOOD
GENERATING SETS
Turbine driven up to 11,000 kw.
Engine driven up to 340 kw.
Hundreds in hand.

PETER BROTHERHOOD
PETERBOROUGH · ENGLAND
COMPRESSOR & POWER PLANT SPECIALISTS FOR NEARLY A CENTURY

also Manufacturers of all kinds of
PLANT TO CUSTOMERS' OWN DESIGNS
WHY NOT SEND YOUR PROBLEMS TO US?
We shall be pleased to investigate them confidentially without commitment

IS YOUR PETROLEUM BOOKSHELF COMPLETE?

It is if it includes ALL the books listed below. Each one is essential to the man who wants to keep abreast of developments and trends in the petroleum industry

- **Reviews of Petroleum Technology**
  VOLUME 12
  Surveying developments during 1950, this volume brings the wide field of petroleum literature within the covers of one book. Price 50s.
  (A few copies of Volumes 10 and 11 are still available at 27s. 6d. each)

- **Oil Shale and Cannel Coal**
  Eight hundred pages of the latest data on all aspects of oil from shale. Price 63s.

- **Electrical Code**
  Covers safety practices in the use of electricity in the field, refinery and storage installation. Price 26s.

- **ASTM/IP Petroleum Measurement Tables**
  BRITISH EDITION
  Authoritative tables for use in computing oil quantities in territories which employ the British system of weights and measures. Price 50s.

- **Petroleum Measurement Manual**
  A companion Volume to the "Tables." Essential to anyone who has to deal with the sampling and measurement of liquid petroleum products. Price 25s.

All the above books can be obtained through a bookseller or direct from

THE INSTITUTE OF PETROLEUM

26 PORTLAND PLACE, LONDON, W.1

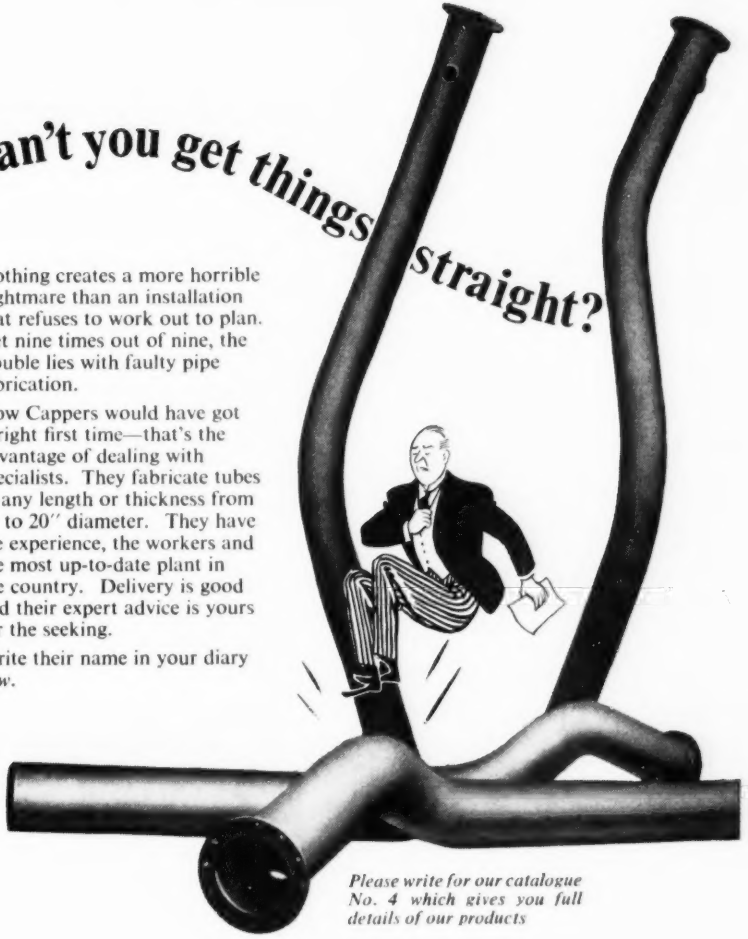
Kindly mention this Journal when communicating with Advertisers

Can't you get things straight?

Nothing creates a more horrible nightmare than an installation that refuses to work out to plan. Yet nine times out of nine, the trouble lies with faulty pipe fabrication.

Now Cappers would have got it right first time—that's the advantage of dealing with specialists. They fabricate tubes of any length or thickness from ⅛" to 20" diameter. They have the experience, the workers and the most up-to-date plant in the country. Delivery is good and their expert advice is yours for the seeking.

Write their name in your diary *now*.



Please write for our catalogue No. 4 which gives you full details of our products

IF IT'S TUBE FABRICATION CONSULT

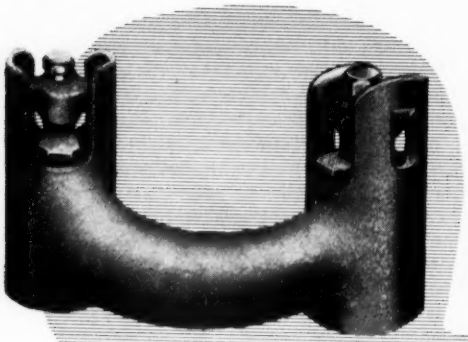
CAPPERS

WILLIAM H. CAPPER & CO. LTD., FORWARD WORKS, WOOLSTON, WARRINGTON
Telephone: Warrington 3266/7/8
London Offices: 20 SOUTHAMPTON PLACE, W.C.1. *Telephone: CHAncery* 4721

Kindly mention this Journal when communicating with Advertisers

OSBORN-OHIO

oil refinery fittings



for EXTRA Service Efficiency

TYPE 1000
MULE EAR FITTINGS

This type of fitting lends itself to the *Directional Solidification* principle of casting, which ensures complete soundness without centre-line weakness and shrinkage.

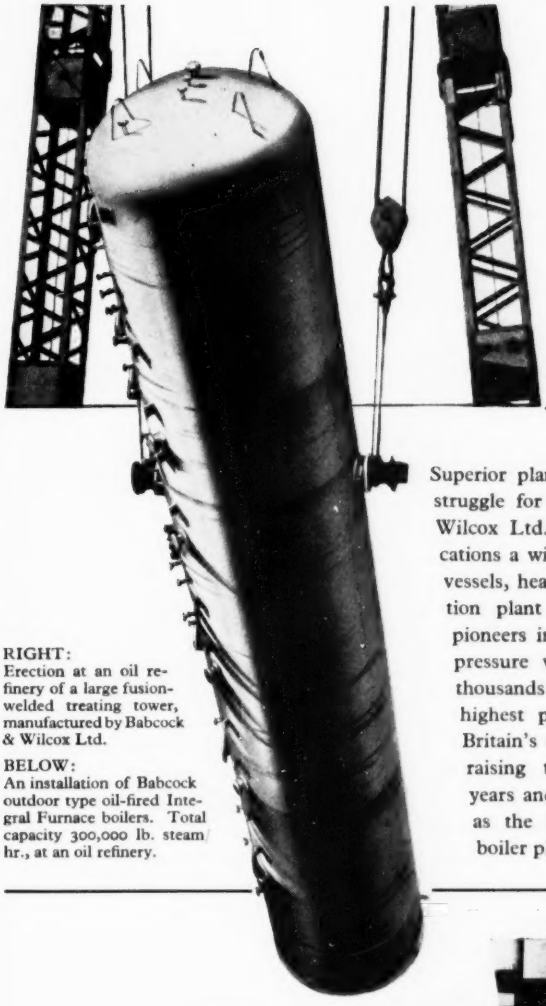
For many years, Osborn Foundry & Engineering Co. Limited, have specialised in the manufacture of Return Bends for Oil Refineries and Chemical Plant. They are cast in many types of steel, for all pipe sizes, are of rugged construction, thoroughly dependable, and will give years of trouble free service.

All Osborn fittings are interchangeable with those made by Ohio Steel Foundry Co., being made in accordance with Ohio designs.

Catalogues will be sent upon request.

OSBORN

SAMUEL OSBORN & CO. LIMITED
CLYDE STEEL WORKS, SHEFFIELD

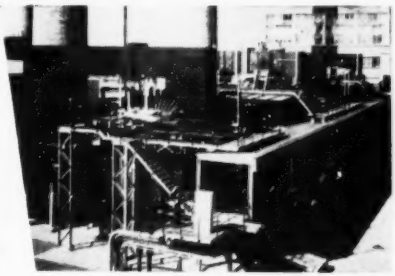


Secret Weapon!

RIGHT:
Erection at an oil refinery of a large fusion-welded treating tower, manufactured by Babcock & Wilcox Ltd.

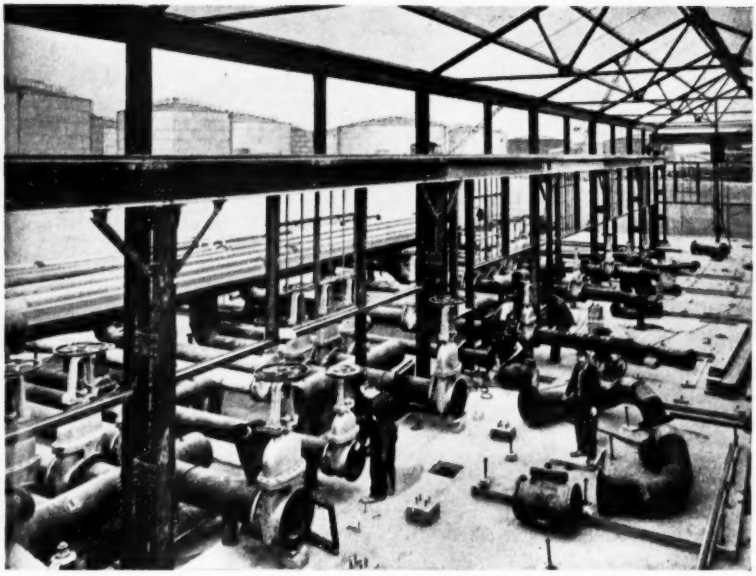
BELOW:
An installation of Babcock outdoor type oil-fired Integral Furnace boilers. Total capacity 300,000 lb. steam/hr., at an oil refinery.

Superior plant is a potent secret weapon in the struggle for economical production. Babcock & Wilcox Ltd. manufacture to the highest specifications a wide range of boilers, welded pressure vessels, heat exchangers, and waste-heat utilisation plant for the oil industry. They were pioneers in the manufacture of fusion-welded pressure vessels, of which they have made thousands in the largest sizes and for the highest pressures, many of these being for Britain's oil refineries. In the field of steam-raising their experience extends over 75 years and they have a world-wide reputation as the leading manufacturers of complete boiler plant.



BABCOCK EQUIPMENT for the OIL INDUSTRY

BABCOCK & WILCOX LTD., BABCOCK HOUSE, FARRINGDON ST., LONDON, E.C.4



THE

MATTHEW HALL

GROUP OF COMPANIES

ESTD. 1848

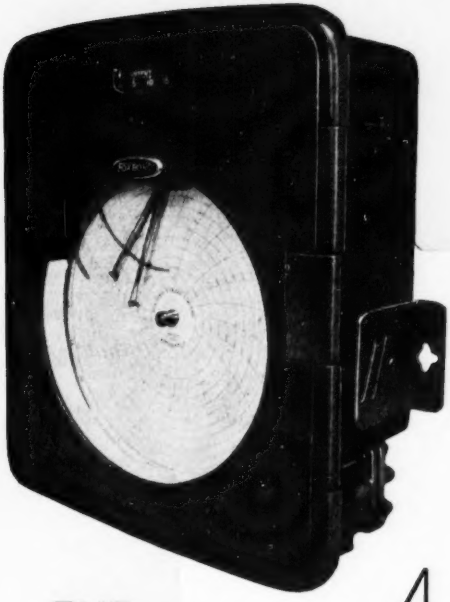
MATTHEW HALL

OIL REFINERY, CHEMICAL AND INDUSTRIAL ENGINEERS
ERECTION OF PLANT AND MACHINERY
WELDED OIL PIPE LINES
AIR CONDITIONING AND REFRIGERATION
FLAMEPROOF ELECTRICAL INSTALLATIONS

THE MATTHEW HALL GROUP OF COMPANIES

MATTHEW HALL & CO. LTD. MATTHEW HALL (PTY.) LTD.
KELCO (METALS) LTD. GARCHEY LTD.

LONDON	36-38 Dorset Square, N.W.1	JOHANNESBURG	53 Commissioner Street	DUBLIN	29 Westland Row
MANCHESTER	95-97 Princess Street	GERMISTON	Wadeville	WEST INDIES	Kingston, Jamaica
GLASGOW	85 & 91 Dyebaud Street, E.2.	DURBAN	180-182 Williams Road	GIBRALTAR	P.O. Box 264
BELFAST	Greenwood Avenue	CAPE TOWN	Rebbeck Square	BULAWAYO	Abercorn House
		WELKOM	Third Street		



THE
FOXBORO
MODEL 40

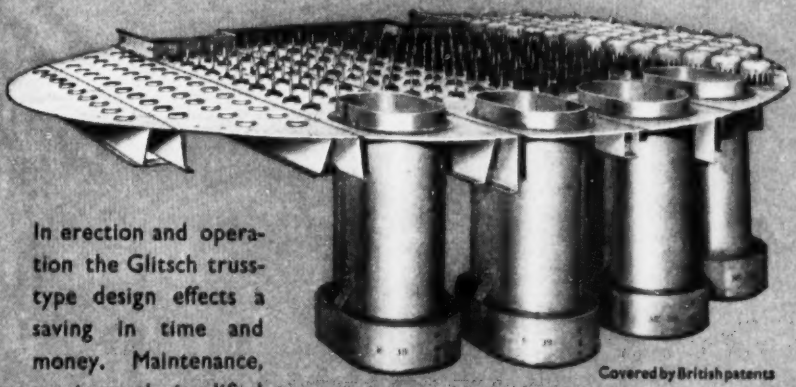
Many years of development and manufacturing experience enable Foxboro to offer the **Model 40 Controller** to satisfy the needs of the varied processes encountered in the Oil and Petroleum Industry where Automatic Control is the key to improved performance and increased quality of product. Complete details about the "**Model 40**" available from

FOXBORO-YOXALL LIMITED
MORDEN ROAD, MERTON, LONDON, S.W.19

EDECO
REGD. TRADE MARK
OIL FIELD EQUIPMENT
ROCK BITS, DRILL COLLARS, SUBSTITUTES, DRAG BITS, SWABS, SLUSH PUMP SPARES
JET NOZZLES AVAILABLE OVER THE FULL 10 TYPE RANGE
VS2 JET TYPE
ENGLISH DRILLING EQUIPMENT CO., LTD.
BILBAO HOUSE, 36-38 NEW BROAD STREET, LONDON, E.C.2
Telephone: LONdon Wall 4941-4
Telegrams: Bullwheel, Ave., London
Subsidiary Companies
EDECO PROSPECTORS, LTD. Batley Works, Fixby, Nr. Huddersfield, Yorks. Tel.: Elland 2876/7
EDECO CANADA, LTD. 10103-80th Avenue, Edmonton, Alberta. Tel.: Edmonton 35025
EDECO (TRINIDAD) LTD. Tel.: San Fernando 2819

Glitsch TRUSS-TYPE

BUBBLE TRAYS



Covered by British patents

In erection and operation the Glitsch truss-type design effects a saving in time and money. Maintenance, too, is greatly simplified and longer runs "on stream" made possible. Refiners throughout the world choose these bubble trays for their economical processing and remarkable flexibility.

METAL PROPELLERS LIMITED

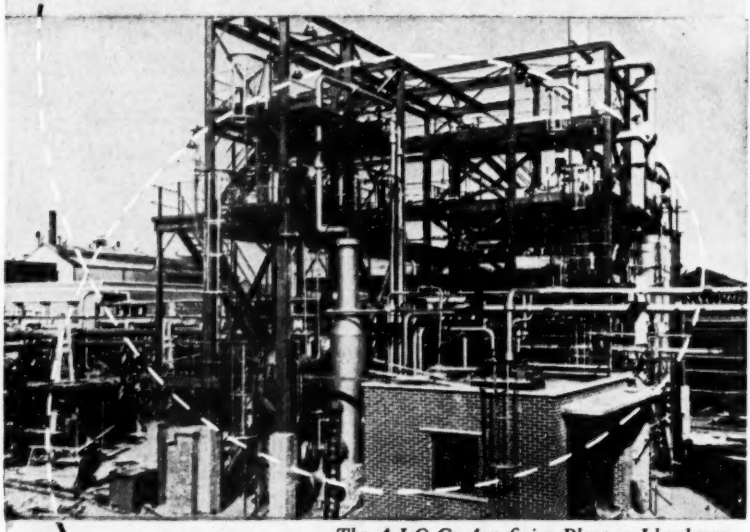
STAINLESS STEEL SPECIALISTS

74 PURLEY WAY CROYDON SURREY

Telephone: Thornton Heath 3411 Telegrams: Metaprops, Souphone, London

CH29

COMPLETE Engineering of Petroleum Chemical and Refinery Plant



The A.I.O.C. Autofining Plant at Llandarcy

From Flow Sheets to Clients' take-over, Frasers offer:—

- ENGINEERING DESIGN,
- FABRICATION of key items in their own works,
- PURCHASING,
- EXPEDITING,
- INSPECTION,
- ERECTION of complete plants.

FRASERS

W. J. FRASER & CO. LTD.
Head Office: Dagenham, Essex.
Works at Dagenham and at Monk Bretton, near Barnsley, S. Yorks.

TAS.PS.394

If you are responsible for the fire safety of oil refinery plant or storage tanks . . .

be sure to obtain the comprehensive information and unrivalled service that we—the largest manufacturers of Mechanical Foam Equipment—can offer.

YOU have a fire safety problem.

WE have a highly experienced staff of Fire Engineers—WHY not let the two combine towards reaching a satisfactory solution . . .

Write now to Dept. J.I.5

THE PYRENE COMPANY LIMITED

9 Grosvenor Gardens, London, S.W.1

Telephone: Victoria 3401

Head Office and Works:
Great West Road, Brentford, Middlesex

Kindly mention this Journal when communicating with Advertisers

Unique

"Newallastic" bolts and studs have qualities which are absolutely unique. They have been tested by every known device, and have been proved to be stronger and more resistant to fatigue than bolts or studs made by the usual method.

C. P. Newall & Co., Ltd.

POSSILPARK GLASGOW · N

Kindly mention this Journal when communicating with Advertisers